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(54) Title: RESIN COMPOSITON FOR RECORDING MATERIAL

(57) Abstract: ABSTRACT The present invention provides a resin composition for a recording material comprising at least one of a resin or its precursor, and at least one of metal particles containing a silver-tin alloy, wherein the amount of silver (Ag) in the metal particles containing a silver-tin alloy is 30 to 80 mole %; a photosensitive transfer material and a light-blocking film for a display device using the resin composition for a recording material; a substrate containing the light-blocking film; and a liquid crystal display element and a liquid crystal display device using the substrate.



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DESCRIPTION

RESIN COMPOSITION FOR RECORDING MATERIAL

TECHNICAL FIELD

The present invention relates to a resin composition containing metal particles for use in a recording material. The present invention further relates to a photosensitive transfer material using the resin composition containing metal particles, a light-blocking film for a display device and a method of forming the same, a substrate containing the light-blocking film, and a liquid crystal display element and a liquid crystal display device using the substrate.

BACKGROUND ART

In recent years, a black matrix, which is a constituent element in color filters, having a high optical density of 4.0 or more have become necessary in order to improve the contrast in display images. On the other hand, if the thickness of a black matrix is large, it becomes necessary to configure a thin membrane since the surface smoothness of the color filter will be lost.

Hitherto, a thin film of metal has been used in the fabrication of a black matrix for a display device having a high light-blocking effect. This method of fabrication is done by providing a thin film of metal such as chromium or the like on a substrate by a vapor deposition method or a sputtering method, coating the thin film of metal with a photo resist, and then, after exposing and developing the photo resist using a photo mask having a pattern for a light-blocking film for the display device, etching the exposed thin film of metal, and finally exfoliating and removing the photo resist remaining on the thin film of metal (see, for example, "Color TFT liquid crystal display," pp. 218-220, published by Kyoritsu Shuppan Co., Ltd., April 10, 1997).

Since this method uses a thin film of metal, a high light-blocking effect is obtained even if the thickness of the film is small, but on the other hand, there is a problem that a vacuum film

forming process, such as a vapor deposition method or a sputtering method, or an etching process becomes necessary, making the cost higher. There is also a problem of extremely high reflectivity because the film is a metal film, so the display contrast is low under intense external light. To solve these problems, a method using low-reflection chromium film (composed of two layers of the metal chromium and chromium oxide) has been proposed, but it undeniably results in a further increase in cost. Furthermore, this method has a large disadvantage in that the environmental burden is large since waste liquid which contains metallic ions is discharged in the etching process. In particular, chromium, which is most frequently used, is toxic and creates an extremely large environmental burden.

On the other hand, as one of the technologies for obtaining a black matrix having a small environmental burden, there is a technology which uses carbon black (see, for example, Japanese Patent Application Laid-Open (JP-A) No. 62-9301). In this technology, a photosensitive resin composition containing carbon black is applied onto a substrate and is dried, and, the dried photosensitive resin composition is exposed to light and developed to fabricate a black matrix.

However, the optical density per coated amount of carbon black is low, and, the film must of course be thicker in order to ensure the desired high light-blocking effect and optical density; for example, in order to obtain an optical density of 4.0, which is the same as in the metal film, the required film thickness will be 1.2 to 1.5 μm . Accordingly, after forming the black matrix, when pixels of red, blue and green are formed, the smoothness of the surface of the color filter is lost due to the unevenness of pixel edges, thereby there is the disadvantage of reduced display quality.

Further, JP-A Nos. 2004-240039 and 2005-17322 disclose methods of using fine metal particles instead of carbon black as methods of obtaining a black matrix having a small environmental burden and a high optical density with a thin film. In these methods, a black matrix having a small environmental burden, and a high optical density with a thin film can be

obtained, but there is a possibility that the reflectivity of this black matrix may be high.

In addition, these metals are known to be black when formed as anisotropic fine particles (see, for example, JP-A No. 2005-17322), and Sn is often selected from the viewpoints of safety and cost. A resist containing Sn anisotropic fine particles is black, has a high light-blocking effect, and can be made thinner (optical density of 4.0 is obtained at 1 μm or less) than a resist containing carbon black. However, the manufacturing process for color filters and the like usually includes a baking process of heating at high temperature (for example, 220 °C), resulting in a change in the quality of the color filter during baking that reduces optical density and cause transparency, and thus the light-blocking effect is mostly lost. This is because the melting point of Sn is 230 °C and oxidation is significantly promoted by baking around this temperature range.

DISCLOSURE OF THE INVENTION

The present invention has been made to solve the problems of the prior art. That is, the present invention provides a resin composition for a recording material having a high density of blackness and high light-blocking effect even when it is a thin film that is capable of displaying a clear image at high contrast, a photosensitive transfer material, a light-blocking film for a display device and a manufacturing method thereof, and a substrate with a light-blocking film, and a liquid crystal display element and a liquid crystal display device capable of displaying a clear image at high contrast.

Generally, although the compounding of metals, starting with the alloying of metals, tends to lower the melting point, it is also possible to avoid a lowering of the melting point depending on the composition ratio of the composite metals (including alloys). According to the present invention, it is possible to obtain blackness if the particle shape is not of high aspect by using a composite metal (including an alloy) of the element Ag and the element Sn, and it is also possible to solve the problems in the process that requires highly precise aspect control as in the

conventional composition of Sn alone.

A first aspect of the present invention is a resin composition for a recording material comprising at least one of a resin or its precursor, and at least one of metal particles containing a silver-tin alloy, wherein the amount of silver (Ag) in the metal particles containing the silver-tin alloy is 30 to 80 mole %.

A second aspect of the present invention is the resin composition for a recording material of the first aspect, wherein at least one of the resin or its precursor is photosensitive.

A third aspect of the present invention is the resin composition for a recording material of the first or second aspect, wherein at least one of the resin or its precursor has a thermosetting property.

A fourth aspect of the present invention is the resin composition for a recording material of any one of the first to third aspects, wherein the resin composition is used in the fabrication of a light-blocking film for a display device.

A fifth aspect of the present invention is the resin composition for a recording material of any one of the first to fourth aspects, further comprising at least one solvent.

A sixth aspect of the present invention is a photosensitive transfer material having, on a provisional support, at least one photosensitive resin layer containing the resin composition for a recording material of any one of the first to fifth aspects.

A seventh aspect of the present invention is a method of forming a light-blocking film for a display device comprising applying the resin composition for a recording material of any one of the first to fifth aspects on a substrate using a slit nozzle.

An eighth aspect of the present invention is a method of forming a light-blocking film for a display device comprising: transferring at least one photosensitive resin layer onto a substrate using the photosensitive transfer material of the sixth aspect; exposing to light at least one photosensitive resin layer that has been transferred onto the substrate; developing the at least

one exposed photosensitive resin layer; and baking the at least one developed photosensitive resin layer.

A ninth aspect of the present invention is a light-blocking film for a display device, the film containing, on a substrate, a resin composition comprising at least one resin and at least one of metal particles containing a silver-tin alloy, wherein the amount of silver (Ag) in the metal particles containing the silver-tin alloy is 30 to 80 mole %.

A tenth aspect of the present invention is the light-blocking film for a display device of the ninth aspect, wherein the resin composition is the resin composition for a recording material of any one of the first to fifth aspects.

An eleventh aspect of the present invention is the light-blocking film for a display device of the ninth or tenth aspect, wherein the metal particles containing a silver-tin alloy are dispersed in the resin.

A twelfth aspect of the present invention is the light-blocking film for a display device of any one of the ninth to eleventh aspects, which is used in a black matrix.

A thirteenth aspect of the present invention is a substrate with a light-blocking film having the light-blocking film for a display device of any one of the ninth to twelfth aspects.

A fourteenth aspect of the present invention is the substrate with a light-blocking film of the thirteenth aspect, wherein the substrate with a light-blocking film is used in the fabrication of a color filter.

A fifteenth aspect of the present invention is a liquid crystal display element comprising the substrate with a light-blocking film of the thirteenth or fourteenth aspect.

A sixteenth aspect of the present invention is a liquid crystal display device comprising the liquid crystal display element of the fifteenth aspect.

The present invention provides a resin composition for a recording material having a high density of blackness, and high light-blocking effect even when it is a thin film that is

capable of displaying a clear image at high contrast, a photosensitive transfer material, a light-blocking film for a display device and a manufacturing method thereof, and a substrate with a light-blocking film, and a liquid crystal display element and a liquid crystal display device capable of displaying a clear image at high contrast.

BEST MODE FOR CARRYING OUT THE INVENTION

Hereinafter, a resin composition for a recording material, a photosensitive transfer material using the resin composition for a recording material, a light-blocking film for a display device and a method of forming the same, a substrate with a light-blocking film, a liquid crystal display element, and a liquid crystal display device will be described in detail.

The resin composition for a recording material of the present invention comprises at least one of a resin and/or its precursor, and metal particles containing a silver-tin alloy, and may further comprise other components depending on the purpose or application if necessary. These components are specifically described hereinafter.

-Metal particles containing a silver-tin alloy-

Metal particles containing a silver-tin alloy of the present invention include particles made of a silver-tin alloy, a silver-tin alloy and other metal component, and a silver-tin alloy and other alloy component.

In the present invention, the metal is defined as specified in Iwanami Scientific and Chemical Dictionary, fourth edition (1987, published by Iwanami Shoten), and the silver-tin alloy in the present invention is a mixture of silver and tin at atomic level, and examples thereof include solid solution, eutectic, compound, intermetallic compound and the like. Alloy is defined, for example, as specified in Iwanami Scientific and Chemical Dictionary, fourth edition (1987, published by Iwanami Shoten).

In the metal particles containing a silver-tin alloy in the present invention, at least a part

thereof is composed of a silver-tin alloy, as confirmed by spectrum measurement on the area of 15 nm $\square$ in the center of each particle by acceleration voltage of 200 kV using, for example, HD-2300 (manufactured by Hitachi Ltd.) and EDS (energy diffusion type X-ray spectrometer, manufactured by Noran).

Metal particles containing a silver-tin alloy have a high density of blackness and an excellent light-blocking effect even when they are a thin film or a small amount, and also have a high thermal stability, and therefore, they can be heat treated at high temperature (for example, 200 °C or more) without spoiling the density of blackness, and can be assured a high and stable light-blocking effect. For example, it is preferably usable in a light-blocking film (so-called black matrix) for a color filter that requires a high light-blocking effect and is generally done by baking.

Metal particles containing a silver-tin alloy in the present invention are obtained by compounding (for example, alloying) of silver (Ag) and tin (Sn), wherein the amount of Ag is 30 to 80 mole %. By controlling the amount of Ag in the specified range, a high density of blackness is obtained while thermal stability at a high temperature region is high and reflectivity of light is suppressed.

In other words, if the amount of Ag is less than 30 mole %, the melting point is lowered, it is likely to be changed by heat, and thermal stability is lowered, and if the amount of Ag exceeds 80 mole %, reflectivity of light becomes higher. The amount of Ag is more preferably 40 to 75 mole %, and most preferably 50 to 75 mole %. In particular, particles in which the amount of Ag is 75 mole %, that is, particles of AgSn alloy are manufactured easily, and obtained particles are stable and preferred.

The resin composition for a recording material of the present invention may comprise only one of metal particles containing a silver-tin alloy, or may comprise two or more of metal particles containing a silver-tin alloy differing in the amount of Ag within the specified range.

Metal particles containing a silver-tin alloy in the present invention may be formed by a

general alloying method by heating, fusing and mixing them in a crucible or the like. However, it is preferred to form the metal particles by a particle reduction method, since there is a difference in the melting point between Ag and Sn, that is, the melting point of Ag is around 900 °C and the melting point of Sn is around 200 °C, and an extra process of microparticulation is required after compounding (or alloying). That is, in the particle reduction method, Ag compound and Sn compound are mixed and reduced, and then, metal Ag and metal Sn are deposited simultaneously at close positions, thus this method achieves compounding (for example, alloying) and pulverization at the same time. Since Ag is easily reduced and tends to deposit faster than Sn, it is preferred to control the deposition timing by forming Ag and/or Sn in complex salt.

Examples of the Ag compound preferably include silver nitrate (AgNO_3), silver acetate ($\text{Ag}(\text{CH}_3\text{COO})$), and silver perchlorate ($\text{AgClO}_4 \cdot \text{H}_2\text{O}$), and silver acetate is particularly preferred.

Examples of the Sn compound preferably include stannous chloride (SnCl_2), stannic chloride (SnCl_4), and stannous acetate ($\text{Ag}(\text{CH}_3\text{COO})_2$), and stannous chloride is particularly preferred.

The reducing method includes a method of using a reducing agent, a method of reducing by electrolysis and the like. In particular, the former method of using a reducing agent is preferred because fine particles can be obtained. The reducing agent includes hydroquinone, catechol, para-amino phenol, para-phenylene diamine, hydroxy acetone and the like. In particular, hydroxy acetone is preferred because it is easily volatile, and less harmful to a display device.

Metal particles containing a silver-tin alloy in the present invention are preferred to be particles having physical properties, particle size and particle shape as specified below.

Metal particles containing a silver-tin alloy in the present invention are preferred to be particles having a melting point in a range of 240 to 400 °C as measured by differential scanning calorimetry (DSC) method. When the melting point is in this range, the metal particles have a

favorable thermal stability as compared with metal Ag (melting point 950 °C) or metal Sn (melting point 230 °C).

Specifically, melting property (melting point) of AgSn alloy is measured by setting a sample of AgSn alloy 20 mg in a measuring cell of DSC (SSC/5200, manufactured by Seiko Instruments Inc.), and cooling the crystallization peak using the DSC by lowering the crystallization temperature from 200 °C to room temperature at a speed of 10 °C/min.

Metal particles containing a silver-tin alloy in the present invention are 20 to 700 nm in number average particle size, more preferably 30 to 200 nm, and particularly preferably 40 to 100 nm. When the number average particle size is in this range, the metal particles have a black hue at any of these particle sizes, unlike metal Sn particles. When the number average particle size exceeds 700 nm, surface properties are poor when a film is formed, and when the number average particle size is less than 20 nm, blackness is decreased, and a yellow tint may be formed.

The number average particle size is measured by using a photograph obtained by transmission electron microscope JEM-2010 (manufactured by JEOL Ltd.) as follows.

Selecting 100 particles, diameter of circle having the same area as that of each particle image is obtained as particle size, and average of particle size of 100 particles is defined as number average particle size. The photograph is taken at a 100,000 times magnification and 200 kV of acceleration voltage.

Particle shape of the metal particles containing a silver-tin alloy in the present invention is not particularly limited, and includes cubic, high aspect, low aspect, acicular and other shape.

As far as the above physical properties, particle size and particle shape are obtained and maintained, in addition to elements (Ag or Sn) forming the metal particles containing a silver-tin alloy, other salts, organic materials or elements (Ca, P, Na, and the like) may be also contained.

In the resin composition for a recording material of the present invention, the amount of metal particles containing a silver-tin alloy may be properly selected depending on the purpose or

application, and from the viewpoint of a high light-blocking effect, it is preferred to be 5 to 20 vol.%, more preferably 7 to 15 vol.%, and most preferably 8 to 15 vol.%, based on the total solid content of composition (by volume). When the amount of metal particles containing a silver-tin alloy is in this range, reflectivity of light is suppressed, a high density of blackness and a high light-blocking effect with a thin film can be obtained. In particular, when used as a light-blocking material in an image display region, such as a black matrix of a color filter, a clear display image at high contrast can be obtained. If the amount of metal particles containing a silver-tin alloy is less than 5 vol.%, reflectivity is too high, and display contrast may be spoiled, and if it exceeds 20 vol.%, thickness of formed film may be more than 1 μm .

The amount of a resin and its precursor mentioned thereafter is preferably 0.3 to 8.0% by mass, more preferably 0.5 to 3.0% by mass based on the total amount (mass) of the resin and its precursor.

-Resin and its precursor-

The resin composition for a recording material of the present invention comprises at least one of resin and its precursor. The resin is a polymer component as a binder, and the precursor of resin is a component constituting the resin when polymerized, and includes so-called monomer and oligomer components.

The resin composition for a recording material of the present invention comprises one or two or more of a resin and its precursor and therefore, is preferably contained in a photosensitive polymerizable composition. For example, by using a photosensitive resin or a photosensitive resin composition of precursor, the resin composition for a recording material of the present invention may be provided with a photosensitive property.

The photosensitive resin composition comprises an alkaline soluble binder (polymer), a photopolymerization initiator, and a monomer (also called photopolymerizable monomer) that obtained by addition polymerization with a light and has an ethylenically unsaturated double

bond.

The photosensitive resin composition is classified into a type developable by an alkaline aqueous solution and a type developable by an organic solvent, and the type developable by an alkaline aqueous solution is preferred from the viewpoints of safety and cost of developer.

The photosensitive resin composition may be either negative type cured in the portion which accepts a radiation such as light, electron ray or the like, or positive type cured in the portion which accepts not a radiation.

The positive type photosensitive resin composition comprises a composition using novolak resin. For example, an alkaline soluble novolak resin has been disclosed in Japanese Patent Application Laid-Open (JP-A) No. 7-43899. Further, positive type photosensitive resin disclosed in JP-A No. 6-148888, that is, a photosensitive resin comprising the alkaline soluble resin disclosed in the publication, 1,2-naphthoquinone diazide sulfonic ester as a photosensitizer, and a mixture with a thermosetting agent disclosed in the publication can be used. In this case, the composition is thermosetting. It is also possible to use the composition disclosed in JP-A No. 5-262850.

The negative type photosensitive resin composition includes a photosensitive resin composed of negative type diazo resin and binder, a photopolymerizable composition, a photosensitive resin composition composed of azide compound and binder, and a cinnamic acid type photosensitive resin composition. What is particularly preferred is a photopolymerizable composition comprising a photopolymerization initiator, a photopolymerizable monomer, and a binder as essential constituent elements. The photopolymerizable composition comprises a polymerizable composition B, a polymerization initiator C, a surfactant, an adhesion aid, or other composition, as disclosed in JP-A No. 11-133600.

For example, as a negative type, a photosensitive resin composition which is developable in an alkaline aqueous solution includes a composition consists mainly of a

carboxylic group-containing binder (an alkaline soluble binder such as an alkaline soluble thermoplastic resin), a photopolymerization initiator, and an ethylenically unsaturated double bond-containing monomer (photopolymerizable monomer) which is obtained by addition polymerization with a light irradiation.

Examples of the alkaline soluble binder include a polymer having a carboxylic radical on a side chain, for example, methacrylic copolymer, acrylic copolymer, itaconic copolymer, crotonic copolymer, maleic copolymer, partially esterified maleic copolymer and the like, which are disclosed in JP-A No. 59-44615, JP-B Nos. 54-34327, 58-12577, and 54-25957, and JP-A Nos. 59-53836 and 59-71048. Further, a cellulose derivative having a carboxylic acid on a side chain may be also used. Besides, a composition obtained by adding cyclic acid anhydride to a polymer having a hydroxy group is also used preferably. Particularly, a copolymer of benzyl (meth)acrylate and (meth)acrylic acid or a multicopolymer of benzyl (meth)acrylate, (meth)acrylic acid or other monomer, which are disclosed in U.S. Patent No. 4,139,391, can be used.

The alkaline soluble binder is preferred to have an acid value in a range of 30 to 400 mg KOH/g, and a weight average molecular weight in a range of 1000 to 300000. Besides, in order to improve various performances such as strength of hardened film, alkaline insoluble polymers may be added within a range not adversely affecting the developing performance and others. The alkaline insoluble polymers include an alcohol soluble nylon or epoxy resin.

The alkaline soluble binder is preferred to be added usually by 10 to 95% by mass, and more preferably 20 to 90% by mass based on the total solid content of the photosensitive resin composition. When the amount of the alkaline soluble binder added is within a range of 10 to 95% by mass, adhesiveness of photosensitive resin layer is not too high, and strength or optical sensitivity of the formed layer is not inferior.

The photopolymerization initiator includes vicinal polyketaldonyl compounds disclosed

in U.S. Patent No. 2,367,660, acyloin ether compound disclosed in U.S. Patent No. 2,448,828, aromatic acyloin compound substituted with α -hydrocarbon disclosed in U.S. Patent No. 2,722,512, polynuclear quinone compounds disclosed in U.S. Patent Nos. 3,046,127 and 2,951,758, combination of triaryl imidazole dimer and p-aminoketone disclosed in U.S. Patent No. 3,549,367, benzothiazole compound and trihalomethyl-s-triazine compound disclosed in JP-B No. 51-48516, trihalomethyl-s-triazine compound disclosed in U.S. Patent No. 4,239,850, and trihalomethyl oxadiazole compound disclosed in U.S. Patent No. 4,212,976. In particular, trihalomethyl-s-triazine, trihalomethyl oxadiazole, and triaryl imidazole dimer are preferred. Besides, a polymerization initiator C disclosed in JP-A No. 11-133600 may be also used preferably.

The photopolymerization initiator may be used either alone or in combination of two or more types, and two or more types may be used preferably.

The content of photopolymerization initiator is generally 0.5 to 20% by mass, and more preferably 1 to 15% by mass based on the total solid content of the photosensitive resin composition.

Specific examples of the photopolymerization initiator include a combination of a diazole based photopolymerization initiator and a triazine based photopolymerization initiator because the exposure sensitivity is high, discoloring such as yellowing is small, and display characteristic is excellent. Among them, a combination of 2-trichloromethyl 5-(p-styryl methyl)-1,3,4-oxadiazole, with 2,4-bis (trichloromethyl)-6-[4-(N,N-diethoxycarbonyl methyl)-3-bromophenyl]-s-triazine is particularly preferred.

The ratio of these photopolymerization initiators is preferably, as ratio by mass of diazole system/triazine system, 95/5 to 20/80, more preferably 90/10 to 30/70, and most preferably 80/20 to 60/40.

The photopolymerization initiators are selected from the compounds disclosed in JP-A

Nos. 1-152449, 1-254918, and 2-153353.

A further preferred example is benzophenone system.

When the rate of metal particles containing a silver-tin alloy in the total solid content of the resin composition for a recording material of the present invention is about 5 to 20 vol.%, similar effects are obtained by mixing coumarin compound into the photopolymerization initiator. Coumarin compound is most preferably 7-[2-[4-(3-hydroxy methyl piperidino)-6-diethyl amino] triazinyl amino]-3-phenyl coumarin.

The ratio of photopolymerization initiator and coumarin compound is preferably, by ratio by mass of photopolymerization initiator/coumarin compound, 20/80 to 80/20, more preferably 30/70 to 70/30, and most preferably 40/60 to 60/40.

However, the photopolymerization initiator usable in the present invention is not particularly limited, and may be properly selected from the known materials.

The photopolymerization initiator is generally added in an amount of 0.5 to 20% by mass, and preferably 1 to 15% by mass based on the total solid content of the photosensitive resin composition. When the amount is within the specified range, lowering of photosensitivity and image intensity can be prevented, and the performance can be enhanced sufficiently.

The photopolymerizable monomer may be a compound of which boiling point is 100 °C or more at normal pressure. Specific examples of the photopolymerizable monomer include monofunctional (meth)acrylates such as polyethylene glycol mono(meth)acrylate, polypropylene glycol mono(meth)acrylate, phenoxy ethyl (meth)acrylate, and the like; and multifunctional (meth)acrylates such as polyethylene glycol di(meth)acrylate, polypropylene glycol di(meth)acrylate, trimethylol ethane triacrylate, trimethylol propane triacrylate, trimethylol propane diacrylate, neopentyl glycol di(meth)acrylate, pentaerythritol tetra(meth)acrylate, pentaerythritol tri(meth)acrylate, dipentaerythritol hexa(meth)acrylate, dipentaerythritol penta(meth)acrylate, hexane diol di(meth)acrylate, trimethylolpropane tri(acryloyloxypropyl)

ether, tri(acryloyloxyethyl) isocyanurate, tri(acryloyloxyethyl) cyanurate, glycerine tri(meth)acrylate, (meth)acrylate obtained by addition reaction of ethylene oxide or propylene oxide to multifunctional alcohols such as trimethylol propane or glycerine.

- Other preferred examples include urethane acrylates disclosed in JP-B Nos. 48-41708 and 50-6034, and JP-A No. 51-37193, and multifunctional acrylates and methacrylates such as polyester acrylates, and epoxy acrylates which are reaction product of epoxy resins with (meth)acrylic acids disclosed in JP-A No. 48-64183, and JP-B Nos. 49-43191 and 52-30490. Among them, particularly preferred examples are trimethylol propane tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, dipentaerythritol hexa(meth)acrylate, and dipentaerythritol penta(meth)acrylate.

The photopolymerizable monomer may be used either alone or in combination of two or more types.

The amount of photopolymerizable monomer is generally 5 to 50% by mass, and preferably 10 to 40% by mass based on the total solid content of photosensitive resin composition. When the amount is within this range, photosensitivity and image intensity are not lowered, and the adhesiveness of photosensitive light-blocking layer is not excessive.

The photosensitive resin composition is preferred to further contain thermopolymerization inhibitor aside from the components mentioned above. Examples of the thermopolymerization inhibitor include aromatic hydroxy compounds such as hydroquinone, p-methoxyphenol, p-t-butyl catechol, 2,6-di-t-butyl-p-cresol, beta-naphthol, pyrogallol, and the like, quinones such as benzoquinone, p-toluquinone, and the like, amines such as naphthyl amine, pyridine, p-toluidine, phenothiazine, and the like, aluminum salt or ammonium salt of N-nitrosophenyl hydroxyl amine, chloranil, nitrobenzene, 4,4'-thiobis (3-methyl-6-t-butyl phenol), 2,2'-methylene bis (4-methyl-6-t-butylphenol), 2-mercaptobenzimidazole and the like.

In the photosensitive resin composition, further, other additives may be added as

required, such as plasticizer, surfactant, adhesion promoter, dispersant, suspension inhibitor, leveling agent, antifoaming agent, flame retardant, brightener, solvent and the like.

The adhesion promoter includes alkyl phenol/ formaldehyde novolak resin, polyvinyl ethyl ether, polyvinyl isobutyl ether, polyvinyl butyral, polyisobutylene, styrene-butadiene copolymer rubber, butyl rubber, vinyl chloride-vinyl acetate copolymer, rubber chloride, acrylic resin adhesive, aromatic, aliphatic or alicyclic petroleum resin, silane coupling agent and the like.

Further, when the metal particles containing a silver-tin alloy in the present invention are used in the form of a dispersion in water, an aqueous photosensitive resin composition system may be used. Such photosensitive resin composition includes the materials mentioned in paragraphs [0015] to [0023] in JP-A No. 8-271727, and commercial products such as SPP-M20 (manufactured by Toyo Gosei Kogyo Co., Ltd.).

-Solvent-

The resin composition for a recording material of the present invention may be composed further preferably by using a solvent.

The solvent is not particularly limited, and examples of the solvent include water, toluene, xylene, methyl ethyl ketone, methyl isobutyl ketone, acetone, methyl alcohol-N-propyl alcohol-1-propyl alcohol, propylene glycol monomethyl ether, propylene glycol monomethyl ether acetate, cyclohexanone, cyclohexanol, ethyl lactate, methyl lactate, caprolactam and the like.

The solvent may be used either alone or in combination of two or more types.

The resin composition for a recording material of the present invention is used for manufacturing a recording material. The "recording material" in the present invention is a material for forming an image by using light, heat, electron ray, electrostatic force, magnetic force, physical force or the like. Specific examples of the recording methods include photolithography, ink jet, silver salt photography and the like, and the recording material is the

material used in these methods.

The resin composition for a recording material (including photosensitive and/or thermosetting material) of the present invention can be preferably used in the manufacture of a light-blocking film for a display devices (for example, a black matrix forming a color filter), and when forming a black matrix, a black matrix having a thin film and a high optical density, and capable of displaying a clear image at high contrast can be obtained.

<Light-blocking film for a display device and method of forming the same, and photosensitive transfer material>

A light-blocking film for a display device of the present invention comprises at least one of resins, and at least one of metal particles (called metal particles in the present invention) containing a silver-tin alloy, wherein the amount of silver (Ag) is 30 to 80 mole %, and may further comprises other components, and may be preferably composed by using the resin composition for a recording material of the present invention. Further, when using the resin composition for a recording material containing precursor of resin, the light-blocking film for a display device may contain unreacted precursor.

The light-blocking film for a display device of the present invention may be formed in any one of methods such as a coating method in which a composition comprising at least one of resins and metal particles of the present invention (preferably, resin composition for a recording material of the present invention) is prepared, and the composition is applied and dried to form a resin layer (including photosensitive layer), and then is patterned, and a transfer method in which a transfer material having a layer of the composition is prepared, the layer is transferred to form a photosensitive layer, and then is patterned. The patterning method is not particularly limited, and its detail is specified below.

The resin layer (including photosensitive resin layer) can be formed by applying the resin composition for a recording material of the present invention according to a known coating

method, and by drying it favorably. In the present invention, it is preferred to use a slit type nozzle having slit holes at the liquid discharge portion when coating.

More specifically, the present invention preferably employs slit type nozzles and slit coaters disclosed in, for example, JP-A Nos. 2004-89851, 2004-17043, 2003-170098, 2003-164787, 2003-10767, 2002-79163, and 2001-310147. Besides, the resin layer may be also formed by applying a solution of the resin composition for a recording material of the present invention using coating machines such as spinner, whirler, roller coater, curtain coater, knife coater, wire bar coater, and extruder, and by drying the layer coated.

When forming a light-blocking film for a display device by a method of forming the light-blocking film for a display device of the present invention, the slit type nozzle or slit coater is preferably used.

In the case of transfer method, the photosensitive resin layer can be formed by transferring the photosensitive resin layer onto a substrate that forms finally the support by using a photosensitive transfer material of the present invention described hereinafter.

-Photosensitive transfer material-

Photosensitive transfer materials used in the transfer method will be explained.

As mentioned above, it is possible to prepare a photosensitive transfer material comprising photosensitive resin layers that are formed by a photosensitive composition comprising metal particles containing a silver-tin alloy, wherein the amount of Ag in the metal particles is in a range of 30 to 80 mole %, and thus, the obtained photosensitive transfer material can be used to form a light-blocking film (black matrix) by transfer method.

The photosensitive transfer material of the present invention comprises a photosensitive resin layer comprising metal particles (wherein the amount of Ag is in a range of 30 to 80 mole %), especially a photosensitive resin layer comprising a resin composition for a recording material of the present invention, and therefore, a light-blocking film having an excellent thermal

stability at a high temperature region, and a high optical density even when it is a thin film can be preferably fabricated.

The photosensitive transfer material comprises a provisional support and a photosensitive resin layer formed thereon by using the resin composition for a recording material of the present invention, and may comprise, as required, a thermoplastic resin layer, an intermediate layer, or a protective film.

Thickness of the photosensitive resin layer is preferably 0.2 to 2 μm , or more preferably 0.2 to 0.9 μm .

The provisional support, thermoplastic resin layer, and intermediate layer are mentioned in paragraphs [0061] to [0070] of JP-A No. 2005-17322, the disclosure of which is incorporated by reference herein.

-Fabrication of photosensitive transfer material-

The photosensitive transfer material of the present invention is manufactured by applying a solution of the photosensitive resin composition for a recording material of the present invention on a provisional support using coating devices such as spinner, whirler, roller coater, curtain coater, knife coater, wire bar coater, extruder, slit coater, or the like, and by drying and forming a photosensitive resin layer. Aside from the photosensitive resin layer, a thermoplastic resin layer, an intermediate layer and other layer can be formed similarly.

-Method of forming a light-blocking film for a display device-

A method of forming a light-blocking film for a display device will be explained.

A light-blocking film for a display device of the present invention (or merely called a light-blocking film) may be fabricated by patterning the composition comprising metal particles of the present invention (preferably resin composition for a recording material of the present invention), or a layer formed by using a photosensitive transfer material of the present invention or a photosensitive resin layer. The patterning method of forming the light-blocking film by using

the composition (preferably the resin composition for a recording material of the present invention) is not particularly limited.

Thickness of the light-blocking film is preferably about 0.2 to 2 μm , or more preferably 0.9 μm or less.

The light-blocking film for a display device of the present invention is preferably a film formed by dispersing metal particles containing a silver-tin alloy of which the amount of Ag is in a range of 30 to 80 mole %, so that a high optical density (4.0 or more) is obtained at a thin film thickness as mentioned above.

The state of metal particles containing a silver-tin alloy during dispersion is not particularly limited, but it is preferred that metal particles containing a silver-tin alloy are present in a stably dispersed state. Examples of dispersant include compound containing a Thiol group, compound containing a polyethylene oxide group, an amino acid and its derivatives, peptide compound, polysaccharides and natural polymers derived from polysaccharides, synthetic polymers and gels derived therefrom, and the like.

In an example of the black matrix as the light-blocking film for a display device, pattern forming methods of black matrix will be explained hereinafter.

In a first method, a photosensitive resin layer comprising metal particles containing a silver-tin alloy of which the amount of Ag is in a range of 30 to 80 mole % (corresponding to metal particles of the present invention) is applied on a substrate, and a photosensitive resin layer comprising metal particles of the present invention is formed as a black material. Thereafter, the photosensitive resin layer is exposed and developed to remove the photosensitive resin except for the portion of pattern forming a black matrix, and thus, patterning is performed to obtain a black matrix. On the photosensitive resin layer, a layer having the same composition as that on an intermediate layer may be formed as a protective layer. For coating, a slit type nozzle or slit coater is used preferably.

In a second method, a non-photosensitive composition comprising metal particles in the present invention is applied on a substrate, and a coated film comprising metal particles in the present invention is formed as a black material. Thereafter, a photosensitive resist liquid is applied on the coated film to form a resist layer, and the resist layer is exposed and developed to form a pattern thereon, and the non-patterned portion (portion which does not form a black matrix) of the coated film is dissolved according to the pattern to form a pattern. Finally, the resist layer is removed, and black matrix is formed.

In a third method, a coated layer is preliminarily formed on a non-patterned portion (portion which does not form a black matrix) presented on a substrate, on which a non-photosensitive composition comprising metal particles of the present invention is applied, and a light-blocking film comprising metal particles of the present invention is formed as a black material. The coated layer preliminarily formed is removed together with a laminated light-blocking film, to form a black matrix.

A fourth method is a method by transfer method using the photosensitive transfer material mentioned above. That is, using the photosensitive transfer material of the present invention mentioned above, at least a photosensitive resin layer is transferred onto a substrate (that forms finally a support), and at least the photosensitive resin is exposed in a pattern, and the exposed photosensitive resin layer is developed, undesired portion (portion which does not form a black matrix as a light-blocking film) is developed and removed, and at least the photosensitive resin layer after developing process is heated and baked.

Specifically, on an optically transparent substrate, a photosensitive transfer material including a photosensitive resin layer comprising metal particles of the present invention is disposed and laminated so as to contact with the photosensitive resin layer of the photosensitive transfer material, and a provisional support is separated from a laminate of the photosensitive transfer material and the optically transparent substrate, then the photosensitive resin layer is

exposed, developed and patterned by way of a photo mask for forming a light-blocking film, and therefore, a black matrix is formed. This method does not require complicated processes, and is low in cost.

In the present invention, a substrate with a light-blocking film can be obtained by forming a black matrix (a light-blocking film) comprising metal particles of the present invention on a substrate, and a color filter can be manufactured by forming coloring pixels of red (R), green (G), or blue (B) on the substrate. Specifically, a color filter can be manufactured by any one of the known methods such as a method in which steps of forming a photosensitive resin layer colored in R, G or B on the substrate, exposing and developing are included and these steps are repeatedly performed by the number of colors.

Method of forming a photosensitive resin layer on a substrate preferably includes (a) a method of applying the resin composition for a recording material of the present invention by known coating methods (coating method), and (b) a method of laminating and transferring the photosensitive resin transfer material of the present invention using a laminator or the like (transfer method).

(a) Coating method

A slit type nozzle or slit coater is used for applying the composition. Preferred examples of the slit type nozzle or slit coater are as mentioned earlier.

(b) Transfer method

In the case of transfer, the photosensitive transfer material of the present invention is used, and a photosensitive resin layer formed in a film is compressed or thermocompressed using heated and/or pressurized roller or flat plate to laminate it onto the substrate, and is further exfoliated and transferred. Specifically, laminators and laminating methods are disclosed in JP-A Nos. 7-110575, 11-77942, 2000-334836, and 2002-148794, and the method described in JP-A No. 7-110575 is preferred from the viewpoint of having less impurities.

As the substrate on which the light-blocking film for a display device is formed, a transparent substrate is preferred, including, for example, soda glass plate having silicon oxide film on the surface, low expansion glass, nonalkaline glass, quartz glass plate, and other known glass plates, or plastic film. Preferably, the substrate may be coupled preliminarily in order to improve adherence with the resin composition for a recording material of the present invention, or photosensitive resin layer in the photosensitive transfer material of the present invention. Coupling is preferably performed by a method disclosed in JP-A No. 2000-39033.

When the photosensitive resin layer is provided, an oxygen blocking film may be further formed on the photosensitive resin layer. As a result, the exposure sensitivity is enhanced, and the oxygen blocking film can have the same composition as that in the intermediate layer of the photosensitive transfer material mentioned above.

Photosensitive resin layer is exposed and developed as follows.

A specific mask is disposed above the photosensitive resin layer formed on the substrate, and the mask is exposed or further above the mask (the side not opposite to the photosensitive resin layer of mask) by way of a thermoplastic resin layer and an intermediate layer is exposed (exposure step), and after the exposure, developing treatment is performed by using a developing solution (developing step).

Light source for the exposure may be properly selected so long as it is possible to emit the light at a spectrum of the wavelength capable of hardening the photosensitive resin layer (for example, 365 nm, 405 nm, and the like). Specific examples of the light sources include superhigh pressure mercury lamp, high pressure mercury lamp, and metal halide lamp. Exposure quantity is usually about 5 to 200 mJ/cm², and preferably about 10 to 100 mJ/cm².

The developing solution is not particularly limited, and specific examples thereof include known developing solution as disclosed, for example, in JP-A No. 5-72724. Preferably, the developing solution is preferred to express a developing behavior so that the photosensitive

resin layer shows solubility, and preferably includes a compound of $pK_a = 7$ to 13 at a concentration of 0.05 to 5 mol/L, or may further contain a small amount of an organic solvent which is miscible with water. The organic solvent which is miscible with water includes methanol, ethanol, 2-propanol, 1-propanol, butanol, diacetone alcohol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol mono-n-butyl ether, benzyl alcohol, acetone, methyl ethyl ketone, cyclohexanone, ϵ -caprolactone, γ -butyrolactone, dimethyl formamide, dimethyl acetamide, hexamethyl phosphoramidate, ethyl lactate, methyl lactate, ϵ -caprolactam, and N-methyl pyrrolidone. Concentration of the organic solvent is preferably 0.1 to 30% by mass.

In the developing solution, a known surfactant may be further added, and concentration of the surfactant added is preferably 0.01 to 10% by mass.

Method of development includes paddle development, shower development, shower and spin development, dip development, and others. Shower development will be explained below.

In the case of shower development, the development solution is showered and applied to the photosensitive resin layer after exposure process, and the uncured portion can be removed. Before development, it is preferred to remove the thermoplastic resin layer and intermediate layer by showering and applying an alkaline solution of photosensitive resin layer having a low solubility. After development, it is preferred to remove residues of development by showering or blowing a detergent, and brushing and rubbing.

Temperature of the developing solution is preferably 20 to 40 °C, and pH of the developing solution is preferably 8 to 13 .

Method of forming a light-blocking film for a display device of the present invention is specifically described by an example which shows forming a black matrix by transfer method, but the present invention is not limited thereto.

A black matrix is preferably manufactured in the procedure comprising transferring a photosensitive resin layer onto a substrate using the photosensitive transfer material mentioned

above, exposing at least one photosensitive resin layer transferred onto the substrate, developing the at least one exposed photosensitive resin layer, and baking at least one developed photosensitive resin layer. Each step is specifically described below.

i) Cleaning of substrate

A nonalkaline glass substrate (hereinafter called substrate) is cleaned preliminarily to remove soil and dirt from the substrate surface before transfer step. For example, glass detergent (trade name: T-SD1, T-SD2, manufactured by Fuji Photo Film Co., Ltd.) adjusted to 25 °C is showered and blown for 20 seconds, while the substrate surface is cleaned by nylon rotary brush, and the surface is finally rinsed by showering purified water.

ii) Silane coupling treatment

To enhance adhesiveness of photosensitive resin layer by laminating in a transfer step described hereinafter, it is preferred to treat the substrate by silane coupling. Silane coupling agent is preferred to have functional groups interacting with the photosensitive resin. Silane coupling solution (i.e., N- β (aminoethyl) γ -aminopropyl trimethoxy silane 0.3 mass % aqueous solution, trade name: KBM603, manufactured by Shin-Etsu Chemical Co., Ltd.) is showered and blown for about 20 seconds, and the surface is showered by purified water. It is then heated to react the photosensitive resin and the silane coupling agent.

A heating bath may be used, but reaction can be promoted by heating preliminarily the substrate using a laminator.

iii) Laminating (transfer step)

The substrate after cleaning and silane coupling treatment is heated for 2 minutes at 100 °C by substrate preliminary heating device, and is transferred to next laminator. It can be laminated uniformly. The photosensitive transfer material is stripped of protective film, and is uniformly laminated on the substrate that has been heated to 100 °C using the laminator at the conditions that a temperature of rubber roller is 130 °C, line pressure is 100 N/cm, and conveying

speed is 2.2 m/min. If the rubber roller temperature is over 150 °C, the transfer material is likely to wrinkle, and if the temperature is below 100 °C, adhesiveness of the photosensitive resin layer may be weak.

iv) Exposing (exposure step)

After removing the provisional support, the substrate is exposed in pattern by proximity type exposure machine having superhigh pressure mercury lamp. If the substrate size is 50 cm or more, it is preferred to expose both the substrate and a mask (quartz exposure mask having image patterns) in vertical upright state in order to prevent deflection of the mask. The resolution is higher when the clearance between the exposure mask surface and the photosensitive resin layer surface is shorter, but since impurities are likely to stick on the surface, it is preferred to be 100 to 300 μm . A preferred exposure quantity is 10 to 80 mJ/cm^2 .

v) Removal of thermoplastic resin layer and intermediate layer

After exposure, the thermoplastic resin layer and the intermediate layer are developed and removed by using a triethanolamine developing solution T-PD1 (containing 2.5% triethanolamine, nonionic surfactant, and polypropylene based antifoaming agent; manufactured by Fuji Photo Film Co., Ltd.). At this time, the condition is set ideally so that the photosensitive resin layer may not be developed at all. It is preferred to supply the developing solution in shower form at the conditions of 30 °C, 50 seconds, and flat nozzle pressure 0.04 MPa.

vi) Development of photosensitive resin layer (developing step)

In succession, the photosensitive resin layer is developed in alkali, and a pattern of black matrix is formed. A preferred example is Na carbonate developing solution T-CD1 (containing 0.06 mol/L sodium hydrocarbonate, sodium carbonate of same concentration, 1 mass % sodium dibutyl naphthalene sulfonate, anionic surfactant, antifoaming agent, and stabilizer; manufactured by Fuji Photo Film Co., Ltd.). The condition is 35 °C, 35 seconds, and cone type nozzle pressure 0.15 MPa, and by showering. The developing solution may also include KOH system or TMAH

system.

vii) Removal of residue

Residue is removed by using, for example, detergent T-SD1 (containing phosphate, silicate, nonionic surfactant, antifoaming agent, and stabilizer; manufactured by Fuji Photo Film Co., Ltd.) or T-SD2 (containing sodium carbonate and phenoxy polyoxy ethylene surfactant; manufactured by Fuji Photo Film Co., Ltd.), and residual portion of the photosensitive resin layer in unexposed area is removed. Condition is 33 °C, 20 seconds, and cone type nozzle pressure 0.02 MPa, by showering and rotation of nylon rotary brush.

viii) Post-exposure

Post-exposure is applied to the substrate on which the pattern is formed by using superhigh pressure mercury lamp at about 500 mJ/cm². As a result, the polymerization effect is enhanced in subsequent baking step, and the sectional shape of black matrix after baking can be adjusted by the quantity of postbaking. It may be also applied from both sides, and the exposure quantity may be selected in a range of 100 to 800 mJ/cm².

ix) Baking (baking step)

Baking is applied to form a hardened film by reaction of monomer or oligomer. Baking condition is preferably 200 to 240 °C, and 10 to 20 minutes approximately. After forming a black matrix, when RGB color pixels are further formed similarly, by baking in the same condition as when forming the black matrix, it is preferred to heat further for 30 to 180 minutes at 200 to 240 °C after forming black matrix and color pixels. The temperature and time is set preferably at higher temperature and shorter time in a range not to cause color changes (yellowing) by baking and lowering of production efficiency.

The light-blocking film (including black matrix) for a display device of the present invention is preferably applied in liquid crystal display device composed of known members as described below.

<Substrate with a light-blocking film>

The substrate with a light-blocking film of the present invention is composed by forming the light-blocking film for a display device of the present invention described above on a substrate. Specifically, on an optically transparent substrate, the layer formed above (including photosensitive resin layer) is patterned by using a resin and/or its precursor, and composition comprising metal particles of the present invention (preferably, resin composition for a recording material of the present invention).

The substrate with a light-blocking film of the present invention is preferably applied in the manufacture of color filter, as a black matrix substrate on which a black matrix (a light-blocking film) is formed.

When formed as a black matrix substrate, the thickness of the light-blocking film is preferably 0.2 to 2.0 μm , or more preferably 0.2 to 0.9 μm . The light-blocking film of the black matrix substrate preferably is formed by dispersing metal particles containing a silver-tin alloy, and a high optical density is obtained even when it is a thin film. Japanese Patent Application Nos. 2005-055137 and 2005-223695 are incorporated herein by reference (in the entirety).

<Liquid crystal display element>

Liquid crystal display elements of the present invention are manufactured by using the substrate with a light-blocking film of the present invention.

One mode of the liquid crystal display elements comprises a liquid crystal layer and a liquid crystal driving means (including a simple matrix driving system and an active matrix driving system) disposed between a pair of substrates (comprising the substrate with a light-blocking film of the present invention) of which at least one is optically transparent.

In this case, the substrate with a light-blocking film of the present invention has plural RGB pixel groups, and each pixel of the pixel groups is mutually formed as a color filter which is separated by a black matrix formed by resin composition for a recording material of the present

invention. This color filter is high in flatness, and a liquid crystal display device having this color filter is suppressed in generation of cell gap unevenness between the color filter and the substrate, free from display failure such as uneven color, and high in contrast, and hence the manufactured liquid crystal display element can display an image clearly.

Other mode of liquid crystal display element comprises a liquid crystal layer and a liquid crystal driving means disposed between a pair of substrates (comprising the substrate with a light-blocking film of the present invention) of which at least one is optically transparent, wherein the liquid crystal driving means has an active element (for example, TFT), and the black matrix formed by using the resin composition for a recording material of the present invention is positioned between the active elements. In this case, the substrate with a light-blocking film has plural RGB pixel groups, and each pixel of the pixel groups is mutually formed as a color filter which is separated by black matrix formed by the resin composition for a recording material of the present invention.

The liquid crystal usable in the liquid crystal display element includes nematic liquid crystal, cholesteric liquid crystal, smectic liquid crystal, ferroelectric liquid crystal and the like.

The pixel group of the color filter may be composed of two different colors, pixels of three colors, or pixels of four colors or more. When the pixel group is composed of three colors, for example, it is composed of three hues of red (R), green (G) and blue (B) colors. Pixel groups of RGB colors may be disposed in mosaic or triangle profile, and pixel groups of four or more colors may be formed in any profile. To manufacture a color filter, a black matrix having pixel groups of two or more colors may be formed as specified below, or a black matrix may be formed first, and pixel groups may be formed later. Forming method of RGB colors is disclosed, for example, in JP-A No. 2004-347831.

The optically transparent substrate includes soda glass substrate having film on the surface, low expansion glass plate, nonalkaline glass plate, quartz glass, and other known glass

plates and plastic films.

<Liquid crystal display device>

Liquid crystal display devices of the present invention are manufactured by comprising the liquid crystal display element of the present invention. Liquid crystal display device is described, for example, in “Next-generation liquid crystal display technology” (edited by Tatsuo Uchida, Sokukogo Chosakai, published in 1994).

The liquid crystal display device of the present invention is not particularly limited as far as the liquid crystal display element of the present invention is used, and the liquid crystal display device may be manufactured in various systems mentioned, for example, in the cited reference of “Next-generation liquid crystal display technology.” In particular, it is effective to compose a liquid crystal display device of color TFT system.

The liquid crystal display device of color TFT system is disclosed, for example, in “Color TFT liquid crystal display” (Kyoritsu Shuppan Co., Ltd., published in 1996).

A liquid crystal display device having an expanded angle of view may be also manufactured, for example, a lateral electric field driving system such as IPS and the like, or a pixel dividing system such as MVA and the like. These systems are disclosed, for example, in page 43 of “EL, PDP, LCD display - technology and recent market trend” (Toray Research Center Investigation and Research Department, published in 2001).

The liquid crystal display device of the present invention is manufactured by using, aside from the liquid crystal display element of the present invention, various general members such as electrode substrate, polarizing film, phase difference film, backlight, spacer, field angle compensation film, anti-reflection film, light diffusion film, and antiglare film. These members are listed, for example, in “‘94 market of peripheral materials and chemicals for liquid crystal displays” (Kentaro Shima, CMC, 1994) and “2003 liquid crystal related market and future outlook” (second volume) (Ryokichi Omote, Fuji Chimera Research Institute, 2003), and types of

LCD include STN, TN, VA, IPS, OCS, R-OCB and the like.

Liquid crystal display devices of the present invention may employ various display modes including ECB (Electrically Controlled Birefringence), TN (Twisted Nematic), IPS (In-Plane Switching), FLC (Ferroelectric Liquid Crystal), OCB (Optically Compensatory Bend), STN (Super Twisted Nematic), VA (Vertically Aligned), HAN (Hybrid Aligned Nematic), and GH (Guest Host). Among these display modes, VA (Vertically Aligned) is most preferable from the viewpoint that the display device of high display quality can be provided.

EXAMPLES

Hereinafter, the present invention will be described with reference to examples, but is not limited thereto. In the following examples, “parts” and “%” refer to parts by mass and % by mass.

(Example 1) Coating method

<Preparation of dispersion solution A1 (dispersion solution of metal particles containing a silver-tin alloy) >

In 1000 ml of purified water, silver (I) acetate 23.1 g, tin (II) acetate 65.1 g, gluconic acid 54 g, sodium pyrophosphate 45 g, polyethylene glycol (molecular weight 3,000) 2 g, and E735 (manufactured by ISP; vinyl pyrrolidone/ vinyl acetate copolymer) 5 g were dissolved, and thus, solution 1 was obtained.

Separately, in 500 ml of purified water, hydroxy acetone 36.1 g was dissolved, and thus, solution 2 was obtained.

The solution 1 obtained above was strongly stirred at a constant temperature of 25 °C, to which the solution 2 was added in 2 minutes, and the mixture was slowly stirred for 6 hours. The mixed solution was changed to black color, and thus, metal particles containing a silver-tin alloy (also called particles containing a silver-tin alloy) were obtained. The solution was then

centrifuged to allow particles containing a silver-tin alloy to precipitate. Centrifugation was performed for 30 minutes at rotating speed of 2,000 r.p.m by dispensing the solution into small portion of 150 ml in TABLETOP CENTRIFUGE H-103N (manufactured by KOKUSAN Co., Ltd.). The supernatant was discarded, and the total liquid volume was adjusted to 150 ml, and 1350 ml of purified water was added, and the mixture was stirred for 15 minutes, and the particles containing a tin-silver alloy were dispersed again. This operation was repeated twice, and soluble material of water phase was removed.

This solution was further centrifuged to precipitate the particles containing a silver-tin alloy again. Centrifugation was performed in the same conditions mentioned above. After centrifugation, the supernatant was discarded similarly, and the total liquid volume was adjusted to 150 ml, and 850 ml of purified water and 500 ml of acetone were added, and the mixture was further stirred for 15 minutes to disperse the particles containing a silver-tin alloy again.

By similar centrifugation again, particles containing a silver-tin alloy were precipitated, and the supernatant was discarded similarly, and the total liquid volume was adjusted to 150 ml, and 150 ml of purified water and 1200 ml of acetone were added, and the mixture was further stirred for 15 minutes to disperse the particles containing a silver-tin alloy again. Centrifugation was performed again. The condition of this centrifugation is the same as above except that the operation time was extended to 90 minutes. The supernatant was discarded, and the total liquid volume was adjusted to 70 ml, and 30 ml of acetone was added. The solution was dispersed for 6 hours using Eiger Mill (Eiger Mill M-50; media: 130 g of zirconia beads having a diameter of 0.65 mm, manufactured by Eiger Japan Co.), and thus, a dispersion solution A1 (a dispersion solution of particles containing a silver-tin alloy) was obtained.

The particles containing a silver-tin alloy were identified to be composite of AgSn alloy ($2\theta = 39.5^\circ$) and Sn metal ($2\theta = 30.5^\circ$) by X-ray scatter. The angles in parentheses are scatter angles of each (III) plane. The fine particle dispersion solution was observed by transmission

electron microscope, and the average particle size of dispersion was about 40 nm in number average particle size.

The number average particle size was measured as follows by using the photographs taken by transmission electron microscope JEM-2010 (manufactured by JEOL Ltd.).

Selecting 100 particles, diameter of circle having the same area as that of each particle image was obtained as particle size, and average of particle size of 100 particles was defined as number average particle size. The photograph is taken at a 100,000 times magnification and 200 kV of acceleration voltage.

<Preparation of photosensitive coating solution for a light-blocking film>

The respective components were mixed with the following composition, and a photosensitive coating solution for a light-blocking film was prepared.

[Composition]

Dispersion solution A1 (Dispersion solution of particles containing a silver-tin alloy),
50.00 parts

Propylene glycol monomethyl ether acetate, 28.6 parts

Methyl ethyl ketone, 37.6 parts

Fluorine based surfactant (F-780-F, manufactured by Dainippon Ink & Chemicals, Ltd.),
0.2 part

Hydroquinone monomethyl ether, 0.001 part

Styrene/acrylic acid copolymer (molar ratio = 56/44, weight average molecular weight
30,000), 9.6 parts

Dipentaerythritol hexacrylate (KAYARAD DPHA, manufactured by NIPPON KAYAKU
CO., LTD.), 9.6 parts

Bis[4-[N-[4-(4,6-bis(trichloromethyl)-s-triazine-2-yl) phenyl]-carbonyl] phenyl]
sebacate, 0.5 part

<Preparation of coating solution for protective layer]

The respective components were mixed with the following composition, and a coating solution for protective layer was prepared.

Polyvinyl alcohol (PVA-205, manufactured by KURARAY CO., LTD.), 3.0 parts

Polyvinyl pyrrolidone (PVP-K30, manufactured by ISP Japan, Ltd.), 1.3 parts

Distilled water, 50.7 parts

Methyl alcohol, 45.0 parts

<Manufacturing of substrate with a light-blocking film by coating>

(1) On a glass substrate, the photosensitive coating solution for a light-blocking film obtained above was applied to a film thickness of 0.65 μm by using a glass substrate coater MH-1600 having slit type nozzles (manufactured by FAS Japan, Ltd.), and was dried for 5 minutes at 100 °C to form a photosensitive layer (coating step). On this photosensitive layer, the coating solution for protective layer was applied by spin coater, such that a dry film thickness is to be 1.5 μm , and was dried for 5 minutes at 100 °C to form a protective layer, and a photosensitive material for a light-blocking film was obtained.

(2) Using a proximity type exposure machine having superhigh pressure mercury lamp (manufactured by Hitachi Electronic Engineering Co., Ltd.), the full surface was exposed in a state of a mask (quartz exposure mask having image patterns) and the photosensitive material for a light-blocking film set in vertical upright state, with a clearance of 200 μm between the mask surface and the surface of the side contacting with the intermediate layer of photosensitive layer in the photosensitive materials for a light-blocking film, and at exposure quantity of 70 mJ/cm^2 (exposure step). The exposed photosensitive material for a light-blocking film was developed by using a developing solution TCD (manufactured by Fuji Photo Film Co., Ltd.; alkaline developing solution) (33 °C, 20 seconds; developing step), and a black matrix was formed on the glass substrate.

The glass substrate on which the black matrix was formed was heated for 60 minutes at 220 °C by a substrate preliminary heating device, and was further heated and baked for 50 minutes at 240 °C (baking step), and a substrate with a light-blocking film was obtained.

(Examples 2 to 6, comparative examples 1 to 3, and comparative example 5): coating method

Dispersion solutions were prepared and substrates with a light-blocking film were fabricated in the same procedure as in example 1, except that the amounts of silver (I) acetate 23.1 g and tin (II) acetate 65.1 g used in the preparation of dispersion solution of particles containing a silver-tin alloy (dispersion solution A1) in example 1 were changed to the amounts [g] shown in Table 1. By X-ray scatter which is the same as in example 1, particles in examples 2 to 5 were identified to be composite composed of AgSn alloy and Sn metal or Ag metal, and particles in example 6 was identified to be AgSn alloy.

Table 1

Unit:g

	Dispersion solution	Silver (I) acetate	Tin (II) acetate
Example 1	A1	23.1	65.1
Example 2	A2	33.5	51.9
Example 3	A3	39.5	44.3
Example 4	A4	46.2	35.8
Example 5	A5	51.4	29.2
Example 6	A6	55.8	23.6
Example 7	A7	58.8	19.8
Example 8	A8	61.2	35.8
Comparative Example 1	B1	7.4	84.9
Comparative Example 2	B2	16.4	73.6
Comparative Example 3	B3	67.0	9.4
Comparative Example 5	B5	0	94.3

(Example 7): transfer method

Dispersion solution A7 was prepared in the same procedure as in example 1, except that the amounts of silver (I) acetate 23.1 g and tin (II) acetate 65.1 g used in the preparation of dispersion solution of particles containing a silver-tin alloy (dispersion solution A1) in example 1

were changed to the amounts [g] shown in Table 1, and a substrate with a light-blocking film was fabricated in the same procedure as in example 1, except that a black matrix was formed by transfer method using a photosensitive transfer material prepared hereinafter, instead of the coating method using coating solution containing dispersion solution A7. By X-ray scatter which is the same as in example 1, particles containing a silver-tin alloy were identified to be composite composed of AgSn alloy and Ag metal.

Hereinafter, the fabrication of a photosensitive transfer material and fabrication of a substrate with a light-blocking film using the photosensitive transfer material will be described.

<Preparation of photosensitive transfer material>

(1) On the surface of polyethylene terephthalate provisional support (PET provisional support) of 75 μm in thickness, a coating solution for thermoplastic resin layer which comprises prescription H1 given below was applied to be a dry film thickness of 5 μm by using a slit type nozzle, and dried for 3 minutes at 100 °C to form a thermoplastic resin layer.

(2) On this thermoplastic resin layer, a coating solution for intermediate layer which comprises the prescription P1 given below was applied to be a dry film thickness of 1.5 μm by using a slit coater, and dried for 3 minutes at 100 °C to form an intermediate layer.

(3) Dispersion solution A7 was prepared in the same procedure as in example 1, except that the amounts of silver (I) acetate 23.1 g and tin (II) acetate 65.1 g used in the preparation of dispersion solution of particles containing a silver-tin alloy (dispersion solution A1) in example 1 were changed to the amounts [g] shown in Table 1, and a photosensitive coating solution for a light-blocking film was prepared in the same procedure as in example 1, except that dispersion solution A1 used in the preparation of photosensitive coating solution for a light-blocking film of example 1 was changed to the dispersion solution A7. The obtained photosensitive coating solution for a light-blocking film was applied further on the intermediate layer to be a dry film thickness of 0.65 μm by using a slit type nozzle, and dried for 5 minutes at 100 °C to form a

photosensitive layer.

Further, on the photosensitive layer, polypropylene film of 12 μm in thickness was compressed to form a protective film. As a result, a photosensitive transfer material having a laminated structure of PET provisional support /thermoplastic resin layer/intermediate layer/photosensitive layer/protective film was manufactured.

(Preparation of coating solution for thermoplastic resin layer)

According to the following prescription H, the respective components were mixed, and a coating solution for thermoplastic resin layer was prepared.

-Prescription H of coating solution for thermoplastic resin layer-

Copolymer of methyl methacrylate/2-ethyl hexyl acrylate/benzyl methacrylate/methacrylic acid (=54/12/5/29 [molar ratio]) (weight average molecular weight 80,000), 58 parts

Copolymer of styrene/acrylic acid (=70/30 [molar ratio]) (weight average molecular weight 7,000), 136 parts

2,2-bis[4-(methacryloxy polyethoxy) phenyl] propane (manufactured by Shin Nakamura Kagaku Kogyo Co., Ltd.; multifunctional acrylate), 90 parts

F-780-F (manufactured by Dainippon Ink & Chemicals, Ltd.) (2-butane 30% solution of fluorine based surfactant), 1 part

Methyl ethyl ketone, 541 parts

1-methoxy-2-propanol, 63 parts

Methyl alcohol, 111 parts

(Preparation of coating solution for intermediate layer)

According to the following prescription P1, the respective components were mixed, and a coating solution for intermediate layer was prepared.

-Prescription P1 of coating solution for intermediate layer-

Polyvinyl alcohol (PVA-205, manufactured by KURARAY Co., LTD.), 3.0 parts

Polyvinyl pyrrolidone (PVP-K30, manufactured by ISP Japan, Ltd.), 1.5 parts

Distilled water, 50.5 parts

Methyl alcohol, 45.0 parts

<Fabrication of substrate with a light-blocking film by transfer method>

(1) A protective film of the photosensitive transfer material obtained above was exfoliated and removed, and the exposed photosensitive layer was overlaid to contact with the surface of a glass substrate (thickness 1.1 mm), and was laminated by using laminator LamicII (manufactured by Hitachi Industries, Ltd.), in the conditions that the temperature of rubber roller is 130 °C, line pressure is 100 N/cm, and conveying speed is 2.2 m/min. The PET provisional support was exfoliated, and photosensitive layer/intermediate layer/thermoplastic resin layer were laminated and transferred in this order on the glass substrate (transfer step).

(2) Using proximity type exposure machine having superhigh pressure mercury lamp (manufactured by Hitachi Electronic Engineering Co.), the full surface was exposed in a state of a mask (quartz exposure mask having image pattern) and the glass substrate disposed so that the mask and the thermoplastic resin layer may be opposite to each other, being set in parallel and vertical upright state, with a clearance of 200 μm between the mask surface and the surface of the side contacting with the intermediate layer of photosensitive layer, and at exposure quantity of 300 mJ/cm^2 from the thermoplastic resin layer side through the mask (exposure step).

(3) After exposure, shower development was performed by injecting KOH developing solution CDK-1 (manufactured by Fuji Film Electronics Materials) for 58 seconds using a flat nozzle from above thermoplastic resin layer in the conditions of 25 °C and nozzle pressure 6.15 MPa, and the thermoplastic resin layer, intermediate layer, and unexposed portion of photosensitive layer were developed and removed to obtain patterns (developing step). Further, at the patterned side of the glass substrate, purified water was injected at pressure of 9.8 MPa by

superhigh pressure cleaning nozzle to remove the residue, and a black matrix was formed on the glass substrate.

(4) The glass substrate on which a black matrix was formed was heated for 60 minutes at 220 °C by substrate preliminary heating device, and was further heated and baked for 50 minutes at 240 °C (baking step), and a substrate with a light-blocking film was fabricated.

(Example 8)

A photosensitive coating solution for a light-blocking film was prepared and a substrate with a light-blocking film was fabricated in the same procedure as in example 1, except that silver (I) hypochlorite was used instead of silver (I) acetate used in the preparation of dispersion solution A1 in example 1, and that dispersion solution A8 was prepared according to the "Preparation of dispersion solution of particles containing a silver-tin alloy (dispersion solution A8)" described hereinafter.

-Preparation of dispersion solution of particles containing a silver-tin alloy (dispersion solution A8)-

In 1000 ml of purified water, silver (I) hypochlorite 61.2 g, tin (II) acetate 35.8 g, sodium pyrophosphate 45 g, polyethylene glycol (molecular weight 3,000) 5 g, and AGRIMER AL-10LC (manufactured by ISP; vinyl pyrrolidone/ vinyl acetate copolymer) 5 g were dissolved, and solution 3 was obtained.

Separately, in 500 ml of purified water, hydroxy acetone 36.1 g was dissolved, and solution 4 was obtained.

The solution 3 obtained above was strongly stirred at a constant temperature of 25 °C, and the solution 4 was added in 7 minutes, and the mixture was slowly stirred for 6 hours. The mixed solution was changed to black color, and thus, fine particles of silver-tin (AgSn) composite were obtained. The solution was centrifuged to allow particles containing a silver-tin alloy to precipitate. Centrifugation was performed for 30 minutes at rotating speed of 2,000 r.p.m by

dispensing the solution into small portion of 150 ml in TABLETOP CENTRIFUGE H-103N (manufactured by KOKUSAN Co., Ltd.). The supernatant was discarded, and the total liquid volume was adjusted to 150 ml, to which 150 ml of acetone was added, and the mixture was stirred for 5 minutes, and further 300 ml of acetone was added and stirred for 5 minutes. In addition, 900 ml of acetone was added, and the mixture was stirred for 30 minutes. The obtained solution was concentrated until the volume was 100 ml by using ultrafiltration module (manufactured by Zartorius Ltd.), and Zartocon Mini (fractional molecular weight 10,000). Filtration speed was 3.0 L/h (filtration area 0.1 m²).

The particles containing a silver-tin alloy were identified to be composite of AgSn alloy and Ag metal by X-ray scatter.

(Comparative example 4)

<Preparation of silver fine particle dispersion solution>

73.5 g of Silver fine particles having an average aspect ratio of 2.2, 1.05 g of Sorsperse 20000 (manufactured by Avicia Co.; dispersant) and 16.4 g of methyl ethyl ketone were mixed. The mixture was dispersed by using ultrasonic generator model US-6000 ccvp (manufactured by Nissei), and silver fine particle dispersion solution having a diameter of 100 nm equivalent to circle was obtained.

<Preparation of photosensitive coating solution for a light-blocking film>

According to the following composition, the respective components were mixed, and a photosensitive coating solution for a light-blocking film was prepared.

[Composition]

Silver fine particle dispersion solution (aspect ratio 2.2), 40.00 parts

Propylene glycol monomethyl ether acetate, 28.6 parts

Methyl ethyl ketone, 37.6 parts

Fluorine based surfactant (20%) (F176PF, manufactured by Dainippon Ink & Chemicals,

Ltd.), 0.2 part

Hydroquinone monomethyl ether, 0.001 part

Benzyl methacrylate/methacrylic acid copolymer (molar ratio=73/27, molecular weight 30,000), 2.1 parts

Bis[4-[N-[4-(4,6-bis(trichloromethyl)-s-triazine-2-yl) phenyl] carbamoyl] phenyl] sebacate, 0.1 part

Dipentaerythritol hexacrylate, added to be volume fraction of Ag particles of 10% in dry film

<Preparation of coating solution for protective layer>

According to the following composition, the respective components were mixed, and a coating solution for protective layer was prepared.

Polyvinyl alcohol (PVA-205, manufactured by KURARAY CO., LTD.), 3.0 parts

Polyvinyl pyrrolidone (PVP-K30, manufactured by ISP Japan, Ltd.), 1.3 parts

Distilled water, 50.7 parts

Methyl alcohol, 45.0 parts

<Fabrication of substrate with a light-blocking film by coating method>

(1) On a glass substrate, the photosensitive coating solution for a light-blocking film obtained above was applied to be a film thickness of 0.65 μm by using a spin coater, and was dried for 5 minutes at 100 °C to form a photosensitive layer. On this photosensitive layer, the coating solution for protective layer was applied by a spin coater, such that a dry film thickness thereof is 1.5 μm , and was dried for 5 minutes at 100 °C to form a protective layer, and a photosensitive material for light-blocking film was fabricated.

(2) Using superhigh pressure mercury lamp, the full surface of the obtained photosensitive material for a light-blocking film was exposed from the coated surface side at exposure quantity of 70 mJ/cm^2 . The exposed photosensitive material for a light-blocking film

was developed by using a developing solution TCD (manufactured by Fuji Photo Film Co., Ltd.; alkaline developing solution) (33 °C, 20 seconds) to form a patterned light-blocking film (black matrix), and then, the light-blocking film was heated (baked) for 40 minutes at 240 °C, and a substrate with a light-blocking film was obtained.

(Comparative example 6)

A substrate with a light-blocking film was fabricated in the following method.

Nonalkaline glass substrate was cleaned by UV cleaning device, brushed and cleaned by using a detergent, and further cleaned ultrasonically in superpurified water. The substrate was heated for 3 minutes at 120 °C to stabilize the surface state. The substrate was then cooled to 23 °C, and coated with coloring photosensitive resin composition K1 composed as specified in Table 2, by using glass substrate coater having a slit type nozzle MH-1600 (manufactured by FAS Japan, Ltd.). Using vacuum dryer VCD (manufactured by TOKYO OKA KOGYO CO., LTD.), a part of solvent was dried for 30 seconds to lose the fluidity of the coated film, and unnecessary coated film around the substrate was removed by EBR (edge bead remover), and the substrate was prebaked for 3 minutes at 120 °C, and a photosensitive resin layer K1 having film thickness of 2.4 μm was formed.

Using proximity type exposure machine having superhigh pressure mercury lamp (manufactured by Hitachi Electronic Engineering Co., Ltd.), the full surface was exposed in a state of a mask (quartz exposure mask having image pattern) and the nonalkaline glass substrate having photosensitive resin layer K1 set in vertical upright, with a clearance of 200 μm between the mask surface and the surface of photosensitive resin layer K1, and at exposure quantity of 300 mJ/cm².

Thereafter, the surface of photosensitive resin layer K1 was uniformly moistened by spraying purified water from shower nozzle, and shower development was preformed by spraying KOH developing solution CDK-1 (alkaline developing solution containing KOH and

nonionic surfactant; manufactured by Fuji Film Electronics Materials, Ltd.) from a flat nozzle for 80 seconds at 23 °C and nozzle pressure of 0.04 MPa, and a black pattern was obtained.

Superpurified water was sprayed to the side of glass substrate on which a black pattern was formed by superhigh pressure cleaning nozzle at pressure of 9.8 MPa to remove the residue, and therefore, a black matrix was formed on the nonalkaline glass substrate. The substrate was heated (baked) for 30 minutes at 220 °C, and a substrate with a light-blocking film was manufactured.

Table 2

Coloring photosensitive resin composition	K1
K pigment dispersed matter 1 (carbon black)	25
Propylene glycol monomethyl ether acetate	8.0
Methyl ethyl ketone	53
Binder 1	9.1
Hydroquinone monomethyl ether	0.002
DPHA solution	4.2
2,4-bis(trichloromethyl)-6-[4-(N,N-diethoxy carbonyl methyl)-3-bromophenyl]-S-triazine	0.16
Surfactant 1	0.044

(Unit: parts)

In Table 2, the composition of K pigment dispersed matter 1, binder 1, DPHA solution, and surfactant 1 is as follows:

- Composition of K pigment dispersed matter 1

Carbon black (Special Black 250, manufactured by Degussa AG), 13.1 parts

5-[3-oxo-2-[4-[3,5-bis(3-diethylaminopropyl aminocarbonyl) phenyl] amino carbonyl] phenyl azo]-butyloyl aminobenzamidazolone, 0.65 part

Polymer [random copolymer of benzyl methacrylate/methacrylic acid (=72/28 molar ratio) (weight-average molecular weight 37,000)], 6.72 parts

Propylene glycol monomethyl ether acetate, 79.53 parts

- Composition of binder 1

Polymer [random copolymer of benzyl methacrylate/methacrylic acid (=78/22 molar

ratio) (weight-average molecular weight 40,000)], 27 parts

Propylene glycol monomethyl ether acetate, 73 parts

-Composition of DPHA solution

Dipentaerythritol hexacrylate (containing polymerization inhibitor MEHQ 500 ppm, trade name: KAYARAD DPHA, manufactured by NIPPON KAYAKU CO., LTD.), 76 parts

Propylene glycol monomethyl ether acetate, 24 parts

- Composition of surfactant 1

Megafac F-780-F (manufactured by Dainippon Ink & Chemicals, Ltd.); copolymer of $C_6F_{13}CH_2CH_2OCOCH=CH_2$ (40 parts), $H(O(CH_3)CHCH_2)_7OCOCH=CH_2$ (55 parts), and $H(OCH_2CH_2)_7OCOCH=CH_2$ (5 parts) (weight-average molecular weight 30,000), 30 parts

Methyl ethyl ketone, 70 parts

(Evaluation)

The substrates with a light-blocking film obtained in examples and comparative examples described above were measured and evaluated as follows. Results of measurement and evaluation are shown in Table 3.

1. Optical density

Optical density of the black matrix after baking was measured in the following method.

Using spectrophotometer UV-2100 (manufactured by Shimadzu Corporation), transmission optical density (OD) of a substrate with a light-blocking film was measured at wavelength 555 nm, and transmission optical density (OD^0) of glass substrates used in these substrates with a light-blocking film was measured similarly. The balance of OD and OD^0 (transmission OD; $OD=OD^0$) was determined as transmission optical density.

2. Film thickness

Film thickness of the black matrix after baking was measured by using contact type surface roughness gauge P-10 (manufactured by TENCOR).

3. Reflectivity

Using a spectrophotometer V-560 (manufactured by JASCO Corporation) combined with an absolute reflectivity measuring apparatus ARV-474 (manufactured by JASCO Corporation), absolute reflectivity of glass substrate side on the substrate with a light-blocking film (the side opposite to the film forming side) was measured to read as reflectivity of substrate with a light-blocking film. It was measured at angle of 5 ° from the vertical direction and at wavelength of 555 nm.

Table 3

		Black material		Content of black material (vol.% in solid content)	Average particle size [μm]	Thickness [μm]	Transmiss ion OD (556nm)	Reflectivity [%]
		Amount of Ag (mol %)	Amount of Sn (mol %)					
Example 1	AgSn	31	69	10	40	0.79	4.0	1.5
Example 2	AgSn	45	55	10	35	0.77	4.0	1.5
Example 3	AgSn	53	47	10	40	0.75	4.0	2
Example 4	AgSn	62	38	10	45	0.74	4.0	2
Example 5	AgSn	69	31	10	40	0.75	4.0	3
Example 6	AgSn	75	25	10	70	0.76	4.0	4
Example 7	AgSn	79	21	10	45	0.78	4.0	4.5
Example 8	AgSn	62	38	10	40	0.75	4.0	2
Comparative Example 1	AgSn	10	90	10	60	0.85	4.0	7
Comparative Example 2	AgSn	22	78	10	50	0.81	4.0	6
Comparative Example 3	AgSn	90	10	10	40	0.81	4.0	7
Comparative Example 4	Ag	100	0	10	50	0.82	4.0	15
Comparative Example 5	Sn	0	100	10	40	1.01	2.5	5
Comparative Example 6	Carbon	-	-	26	-	1.4	4.0	0.2

As apparent from Table 3, in the examples using particles containing a silver-tin alloy with Ag ratio of 30 to 80%, light-blocking effect was not spoiled due to baking, a high density of blackness was obtained even when it is a thin film, and reflectivity was excellent.

By contrast, in comparative examples 1 to 3 using particles of which Ag ratio is out of the specified range, although a high density of blackness was obtained even when it is a thin film,

the reflectivity was too high, and therefore, it was inferior from the viewpoint of reflectivity characteristic. Comparative example 4 using Ag particles, which are particles containing no a silver-tin alloy shows that the substrate with a light-blocking film was inferior in reflectivity characteristic, and comparative example 5 using Sn particles shows that the substrate with a light-blocking film was lowered in transmission OD due to baking, and lost light-blocking effect. When carbon black was used as a black material as in comparative example 6, it was hard to obtain same transmission OD as in examples using a thin film.

(Example 9): liquid crystal display device

A substrate with a light-blocking film was obtained in accordance with the same procedure as in example 1, and using the obtained substrate with a light-blocking film, a liquid crystal display device was manufactured as follows.

Pattern of black matrix in the substrate with a light-blocking film has pixel size of 10 inches and number of pixels of 480×640 . Width of black matrix was $24 \mu\text{m}$, and aperture of pixel portion was $86 \mu\text{m} \times 304 \mu\text{m}$.

<Fabrication of photosensitive transfer material>

Coloring photosensitive resin compositions R1, G1, B1 of which each composition was specified in Table 4 were prepared. Then, photosensitive transfer material R1 for forming red pixels, a photosensitive transfer material G1 for forming green pixels, and a photosensitive transfer material B1 for forming blue pixels were fabricated in the laminated structure of PET provisional support /thermoplastic resin layer/intermediate layer/photosensitive layer (R1, G1 or B1)/protective film, according to the same manner as in example 7, except that the photosensitive coating solution for a light-blocking film used in the fabrication of photosensitive transfer material of example 7 was replaced with the coloring photosensitive resin composition R1, G1 or B1.

Table 4

Unit: parts

Coloring photosensitive resin composition	R1	G1	B1
K pigment dispersed matter 1	-	-	-
R pigment dispersed matter 1 (C. I. P. R. 254)	44	-	-
R pigment dispersed matter 2 (C. I. P. R. 177)	5.0	-	-
G pigment dispersed matter 1 (C. I. P. G 36)	-	24	-
Y pigment dispersed matter 1 (C. I. P. Y. 150)	-	13	-
B pigment dispersed matter 1 (C. I. P. B 15:6)	-	-	7.2
B pigment dispersed matter 2 (C. I. P. B 15:6+C. I. P. V. 23)	-	-	13
Propylene glycol monomethyl ether acetate	7.6	29	23
Methyl ethyl ketone	37	26	35
Cyclohexanone	-	1.3	-
Binder 1	-	3	-
Binder 2	0.76	-	-
Binder 3	-	-	17.3
DPHA solution	4.4	4.3	3.8
2-trichloromethyl 5-(p-styryl styryl)-1,3,4-oxadiazole	0.13	0.15	0.15
2,4-bis (trichloromethyl)-6-[4-(N, N-diethoxy carbonyl methyl)-3-bromophenyl]-s-triazine	0.06	0.06	-
Phenothiazine	0.01	0.005	0.02
Hydroquinone monomethyl ether	-	-	-
ED152	0.52	-	-
Surfactant 1	0.03	0.07	0.05

* Detail of each composition is described hereinafter.

<Manufacture of liquid crystal display device>

-Forming of red (R) pixels-

Steps of transfer, exposure, development and baking were performed in the same manner as in example 7, except that the photosensitive transfer material was changed to the photosensitive transfer material R1 obtained above, in the fabrication of substrate with a

light-blocking film of example 7, and red pixels (R pixels) were formed on the black matrix side of the substrate with a light-blocking film. However, in exposure step, the exposure quantity was 40 mJ/cm^2 , in developing step, the condition was 35°C and 35 second, and in baking step, the condition was 220°C and 20 minutes.

Thickness of photosensitive layer R1 was $2.0 \mu\text{m}$, and coating amounts of C.I. Pigment Red (C.I.P.R.) 254 and C.I.P.R. 177 were respectively 0.88 g/m^2 and 0.22 g/m^2 .

The substrate with a light-blocking film on which R pixels were formed was brushed and washed with a detergent as mentioned above, and showered and cleaned by purified water, and heated for 2 minutes at 100°C by using a substrate preheating device without using a silane coupling liquid.

-Forming of green (G) pixels-

Steps of transfer, exposure, development and baking were executed by using photosensitive transfer material G1 in the same manner as when forming R pixels, and green pixels (G pixels) were formed on the black matrix side and red pixel side of the substrate with a light-blocking film. However, in exposure step, the exposure quantity was 40 mJ/cm^2 , in developing step, the condition was 34°C and 45 seconds, and in baking step, the condition was 220°C and 20 minutes.

Thickness of photosensitive layer G1 was $2.0 \mu\text{m}$, and coating amounts of C.I. Pigment Green (C.I.P.G.) 36 and C.I. Pigment Yellow (C.I.P.Y.) 150 were respectively 1.12 g/m^2 and 0.48 g/m^2 .

The substrate with a light-blocking film on which R pixels and G pixels were formed was brushed and washed with a detergent as mentioned above, and showered and cleaned by purified water, and heated for 2 minutes at 100°C by using a substrate preheating device without using a silane coupling liquid.

-Forming of blue (B) pixels-

Steps of transfer, exposure, and development (except baking) were executed by using photosensitive transfer material B1 in the same manner as when forming R pixels and G pixels, and blue pixels (B pixels) were formed at the black matrix side and at the side on which R pixel and G pixel were formed of the substrate with a light-blocking film. However, in exposure step, the exposure quantity was 30 mJ/cm^2 , and in developing step, the condition was 36°C and 40 seconds.

Thickness of photosensitive layer B1 was $2.0 \mu\text{m}$, and coating amounts of C.I. Pigment Blue (C.I.P.B.) 15:6 and C.I. Pigment Violet (C.I.P.V.) 23 were respectively 0.63 g/m^2 and 0.07 g/m^2 .

After forming B pixels, the substrate with a light-blocking film on which each R, G and B pixels was formed was further heated for 50 minutes at 240°C , and a desired color filter substrate was obtained.

Preparation of coloring photosensitive resin compositions R1, G1, and B1 specified in Table 4 will be described below.

(Preparation of coloring photosensitive resin composition R1)

Coloring photosensitive resin composition R1 was prepared as follows: R pigment dispersed matter 1, R pigment dispersed matter 2, and propylene glycol monomethyl ether acetate were weighed and dispersed as specified in Table 4, and were mixed at 24°C ($\pm 2^\circ\text{C}$), and the mixture was stirred for 10 minutes at 150 r.p.m, to which methyl ethyl ketone, binder 2, DPHA solution, 2-trichloromethyl-5-(p-styryl styryl)-1,3,4-oxadiazole, 2,4-bis(trichloromethyl)-6-[4-(N,N-diethoxy carbonyl methyl)-3-bromophenyl]-s-triazine, and phenothiazine weighed as specified in Table 4 were added sequentially in this order at 24°C ($\pm 2^\circ\text{C}$), and then, the mixture was stirred for 30 minutes at 150 r.p.m, and ED152 weighed as specified in Table 4 was added and mixed at 24°C ($\pm 2^\circ\text{C}$), and the mixture was stirred for 20 minutes at 150 r.p.m. Moreover, surfactant 1 was weighed as specified in Table 4, and added at

24 °C (± 2 °C), and the mixture was stirred for 30 minutes at 30 r.p.m, and filtered by nylon mesh #200.

Detail of each composition R1 in the composition shown in Table 4 is specified below.

- Composition of R pigment dispersed matter 1

C.I. Pigment Red 254, 8.0 parts

N,N'-bis-(3-diethylamino propyl)-5-{4-[2-oxo-1-(2-oxo-2,3-dihydro-1H-benzimidazol-5-ylcarbamoyl)-propylazo]-benzoyl amino}-isophthalamide, 0.8 part

Polymer [random copolymer of benzyl methacrylate/methacrylic acid (=72/28 molar ratio) (weight-average molecular weight 37,000)], 8 parts

Propylene glycol monomethyl ether acetate, 83.2 parts

- Composition of R pigment dispersed matter 2

C.I. Pigment Red 177, 18 parts

Polymer [random copolymer of benzyl methacrylate/methacrylic acid (=72/28 molar ratio) (weight-average molecular weight 37,000)], 12 parts

Propylene glycol monomethyl ether acetate, 70 parts

- Composition of binder 2

Random copolymer of benzyl methacrylate/methacrylic acid/methyl methacrylate (=38/25/37 molar ratio) (weight-average molecular weight 30,000)], 27 parts

Propylene glycol monomethyl ether acetate, 73 parts

- Composition of DPHA solution

Dipentaerythritol hexacrylate (containing polymerization inhibitor MEHQ 5000 ppm, trade name: KAYARAD DPHA, manufactured by NIPPON KAYAKU CO., LTD.), 76 parts

Propylene glycol monomethyl ether acetate, 24 parts

- Composition of surfactant 1

Copolymer of $C_6F_{13}CH_2CH_2OCOCH=CH_2$ (40 parts), $H(O(CH_3)CHCH_2)_7OCOCH=CH_2$ (55 parts), and $H(OCH_2CH_2)_7OCOCH=CH_2$ (5 parts) (weight-average molecular weight 30,000), 30 parts

Methyl ethyl ketone, 70 parts

- ED152

HIPLAAD ED152 (manufactured by KUSUMOTO CHEMICALS LTD.)

(Preparation of coloring photosensitive resin composition G1)

Coloring photosensitive resin composition G1 was prepared as follows:

G pigment dispersed matter 1, Y pigment dispersed matter 1, and propylene glycol monomethyl ether acetate were weighed as specified in Table 4 and mixed at 24 °C (± 2 °C), and the mixture was stirred for 10 minutes at 150 r.p.m, to which, methyl ethyl ketone, cyclohexane, binder 1, DPHA solution, 2-trichloromethyl-5-(p-styryl styryl)-1,3,4-oxadiazole, 2,4-bis(trichloromethyl)-6-[4-(N,N-diethoxy carbonyl methyl)-3-bromophenyl]-s-triazine, and phenothiazine further weighed as specified in Table 4 were added sequentially in this order at 24 °C (± 2 °C), and the mixture was stirred for 30 minutes at 150 r.p.m, and then, surfactant 1 was weighed as specified in Table 4 and added at 24 °C (± 2 °C), and the mixture was stirred for 5 minutes at 30 r.p.m, and filtered by nylon mesh #200.

Detail of each composition G1 in the composition shown in Table 4 is specified below.

- Composition of G pigment dispersed matter 1

C.I. Pigment Green 36, 18 parts

Polymer [random copolymer of benzyl methacrylate/methacrylic acid (=72/28 molar ratio) (weight-average molecular weight 37,000)], 12 parts

Cyclohexanone, 35 parts

Propylene glycol monomethyl ether acetate, 35 parts

- Composition of Y pigment dispersed matter 1

Trade name: CF Yellow EX3393 (manufactured by Mikuni Color Ltd.)

- Composition of binder 1

Random copolymer of benzyl methacrylate/methacrylic acid (= 78/22 molar ratio) (weight-average molecular weight 44,000)], 27 parts

Propylene glycol monomethyl ether acetate, 73 parts

(Preparation of coloring photosensitive resin composition B1)

Coloring photosensitive resin composition B1 was prepared as follows:

B pigment dispersed matter 1, B pigment dispersed matter 2, and propylene glycol monomethyl ether acetate were weighed as specified in Table 4 and mixed at 24 °C (± 2 °C), and the mixture was stirred for 10 minutes at 150 r.p.m, to which methyl ethyl ketone, binder 3, DPHA solution, 2-trichloromethyl-5-(p-styryl styryl)-1,3,4-oxadiazole, and phenothiazine further weighed as specified in Table 4 were added sequentially in this order at 25 °C (± 2 °C), and the mixture was stirred for 30 minutes at 150 r.p.m and at 40 °C (± 2 °C), and then, surfactant 1 was weighed as specified in Table 4 and added at 24 °C (± 2 °C), and the mixture was stirred for 5 minutes at 30 r.p.m and filtered by nylon mesh #200.

Detail of each composition B1 in the composition shown in Table 4 is specified below.

- Composition of B pigment dispersed matter 1

Trade name: CF Blue EX3357 (manufactured by Mikuni Color Ltd.)

- Composition of B pigment dispersed matter 2

Trade name: CF Blue EX3383 (manufactured by Mikuni Color Ltd.)

- Composition of binder 3

Random copolymer of benzyl methacrylate/methacrylic acid/methyl methacrylate (= 36/22/42 molar ratio) (weight-average molecular weight 30,000)], 27 parts

Propylene glycol monomethyl ether acetate, 73 parts

-Fabrication of liquid crystal display device-

On the R pixels, G pixels, B pixels and black matrix on a color filter substrate obtained above, transparent electrode of ITO (Indium Tin Oxide) was formed by sputtering. As counter substrate, separately, a glass substrate was used, and the transparent electrode of color filter substrate and counter substrate were patterned for PVA mode, and an orientation film of polyimide was further formed thereon.

At the position corresponding to an outer frame of the black matrix provided in the surrounding to enclose the pixel groups of the color filter, a sealing agent of epoxy resin was printed, liquid crystal for PVA mode was dropped, and it was adhered to the counter substrate at pressure of 10 kg/cm^2 , and the glued substrate was heated and the sealing agent was hardened. On both sides of the liquid crystal cell obtained above, polarizing plates HLC2-2518 (manufactured by SANRITZ CORPORATION) was adhered. Using FR1112H (chip LED manufactured by STANLEY ELECTRIC CO., LTD.) as red (R) LED, DG1112H (chip LED manufactured by STANLEY ELECTRIC CO., LTD.) as green (G) LED, and DB1112H (chip LED manufactured by STANLEY ELECTRIC CO., LTD.) as blue (B) LED, a backlight of side light type was formed, and disposed at the back side of the liquid crystal cell forming the polarizing plate. At the front side viewed by the observer of the liquid Crystal cell, anti-reflection film was adhered, and a liquid crystal display device was manufactured.

The obtained liquid crystal display element was small in reflection by black matrix, high in contrast, and capable of obtaining clear display image.

In the examples, the liquid crystal display device was manufactured by using the substrate with a light-blocking film manufactured in the same manner as in example 1, but when the liquid crystal display device is manufactured by using the substrate with a light-blocking film manufactured in examples 2 to 7, it is capable of obtaining clear display images, is small in reflection by black matrix and is high in contrast.

INDUSTRIAL APPLICABILITY

The resin composition for a recording material of the present invention is used for manufacturing a recording material. As specific recording method, it is used in photolithography, ink jet, silver salt photography or the like. The resin composition for a recording material of the present invention (including photosensitive and/or thermosetting material) is preferably used in manufacture of a light-blocking film for a display device (for example, black matrix forming a color filter and the like), and when a black matrix is formed, the present invention provides liquid crystal display elements and liquid crystal display devices which have a high optical density even when it is a thin film, and are capable of displaying images clearly and at high contrast.

CLAIMS

1. A resin composition for a recording material comprising at least one of a resin or its precursor, and at least one of metal particles containing a silver-tin alloy, wherein the amount of silver (Ag) in the metal particles containing a silver-tin alloy is 30 to 80 mole %.

2. The resin composition for a recording material of claim 1, wherein at least one of the resin or its precursor is photosensitive.

3. The resin composition for a recording material of claim 1, wherein at least one of the resin or its precursor has a thermosetting property.

4. The resin composition for a recording material of claim 2, wherein at least one of the resin or its precursor has a thermosetting property.

5. The resin composition for a recording material of claim 1, wherein the resin composition is used in the fabrication of a light-blocking film for a display device.

6. The resin composition for a recording material of claim 1, further comprising at least one solvent.

7. A photosensitive transfer material having, on a provisional support, at least one photosensitive resin layer containing the resin composition for a recording material of claim 1 or claim 2.

8. A method of forming a light-blocking film for a display device comprising applying the resin composition for a recording material of claim 1 on a substrate using a slit nozzle.

9. A method of forming a light-blocking film for a display device comprising:
transferring at least one photosensitive resin layer onto a substrate using the photosensitive transfer material of claim 7,

exposing to light at least one photosensitive resin layer that has been transferred onto the substrate,

developing the at least one exposed photosensitive resin layer, and

baking the at least one developed photosensitive resin layer.

10. A light-blocking film for a display device, the film containing, on a substrate, a resin composition comprising at least one resin and at least one of metal particles containing a silver-tin alloy, wherein the amount of silver (Ag) in the metal particles containing the silver-tin alloy is 30 to 80 mole %.

11. The light-blocking film for a display device of claim 9, wherein the resin composition is the resin composition for a recording material of claim 1.

12. The light-blocking film for a display device of claim 9, wherein the resin composition is the resin composition for a recording material of claim 2.

13. The light-blocking film for a display device of claim 10, wherein the metal particles containing a silver-tin alloy are dispersed in resin.

14. The light-blocking film for a display device of claim 10, which is used in a black matrix.

15. A substrate with a light-blocking film comprising the light-blocking film for a display device of claim 10.

16. The substrate with a light-blocking film of claim 15, wherein the substrate with a light-blocking film is used in the fabrication of a color filter.

17. A liquid crystal display element comprising the substrate with a light-blocking film of claim 15.

18. A liquid crystal display element comprising the substrate with a light-blocking film of claim 16.

19. A liquid crystal display device comprising the liquid crystal display element of claim 17.

20. A liquid crystal display device comprising the liquid crystal display element of claim 18.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2006/304027

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. C08L101/00 (2006.01), G02B5/20 (2006.01), G02F1/1335 (2006.01),
G03F7/004 (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl. C08L1/00-101/00, G02B5/20, G02F1/1335, G03F7/004

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2006
Registered utility model specifications of Japan 1996-2006
Published registered utility model applications of Japan 1994-2006

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CA (STN)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, A	JP 2005-179632 A (FUJI PHOTO FILM CO., LTD.) 2005.07.07, CLAIMS & US 2005/0112364 A1 & CN 1621916 A	1-20
A	WO 2002/067056 A1 (ZEON CORPORATION) 2002.08.29, CLAIMS & JP 2002-244294 A & KR 2004012682 A	1-20
A	JP 2002-107921 A (NIPPON SHOKUBAI CO., LTD.) 2002.04.10, CLAIMS (FAMILY:NONE)	1-20
A	JP 2002-47423 A (TORAY INDUSTRIES, INC.) 2002.02.12, CLAIMS (FAMILY:NONE)	1-20
A	JP 2000-3047 A (NIPPON PAINT CO., LTD.) 2000.01.07, CLAIMS (FAMILY:NONE)	1-20

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

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"&" document member of the same patent family

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