

DESCRIPTION

COLORED RESIN COMPOSITION AND RESIN BLACK MATRIX SUBSTRATE

TECHNICAL FIELD

[0001]

5 The present invention relates to a colored resin composition and resin black matrix substrate using the same.

BACKGROUND ART

[0002]

10 Light-shielding materials presently have a wide range of applications. In flat panel displays (FPD) such as liquid crystal displays (hereinafter referred to as "LCD" for short) and plasma display panels (hereinafter referred to as "PDP" for short), light-shielding materials are used in gaps of coloring patterns in display areas and in peripheries of display areas for improving the display property of color filters, and used to form a light-shielding image on the side of outside light in TFT.

15 [0003]

 Color filters for LCD are generally produced by a method in which, on the surface of a transparent substrate in which a black matrix is formed such as glass or a plastic sheet, different hues of red, green, and blue are sequentially formed in a color pattern such as stripes or mosaic. The black matrix used as the light-shielding film serves to prevent the decrease in contrast and color purity due to light leakage between pixels.

[0004]

25 Also in substrates for touch panels, a black matrix is formed likewise as a light-shielding film, and is generally formed with a printing ink on a cover glass or cover film facing a sensor substrate. On the other hand, in accordance with an increasing demand to lighten the touch panels, techniques to simultaneously form a light-shielding film and touch sensors on a cover glass are now being developed. In

such a case, it is necessary to form electrodes and the like after forming a black matrix, and, accordingly, high adhesion and chemical resistance as well as high insulation properties are required. Particularly, while alkali-free glass is used as the glass substrate in color filter application, a soda glass substrate containing a large amount of ionic impurities is used as the glass substrate in touch panel application.

5 [0005]

Conventionally, films on which a metal such as chromium, nickel, or aluminum or a metal compound is deposited have been used as a black matrix, but they have problems in that, for example, the process is complicated and costly, and the surface of the metallized thin film is highly reflective. Thus, as a method that can solve these problems, the pigment dispersion method which uses a resin composition in which pigments are dispersed is currently predominant.

10 [0006]

In the pigment dispersion method, among negative and positive photosensitive compositions, negative photosensitive compositions mainly composed of acryl polymer, acrylic polyfunctional monomer or oligomer, photoinitiators, solvents, and pigments have been widely used. As a light-shielding material, carbon black, titanium black such as low-valent titanium oxide and titanium nitride oxide, metal oxides such as iron oxide, and, in addition, mixtures of organic pigments have been used, and carbon black and titanium nitride oxide are predominant. To obtain a black matrix having high insulation properties, titanium black or carbon black whose surface is treated with a resin or the like, or those mixed with an organic pigment have been used as a light-shielding material (Patent Document 1).

15 20 25

[0007]

To promote the adhesion of the black matrix with the substrate, techniques are known wherein at least one selected from the group consisting of amine-

containing silane compounds, ketimine-containing silane compounds and isocyanate-containing silane compounds is added (Patent Document 2) and wherein a silane coupling agent having an ureido group is added (Patent Document 3). However, in cases where soda glass is used as the substrate, a sufficient adhesion is not obtained, and there are problems in that the black matrix is peeled by a treatment under a high temperature and high humidity, or by a treatment with a chemical such as aqua regia or an amine-containing peeling liquid. On the other hand, a silane coupling agent having an imido group has been proposed for a hard coating agent in order to promote adhesion (Patent Document 4, Patent Document 5), the adhesion to the soda glass for touch panels was insufficient.

PRIOR ART DOCUMENTS

PATENT DOCUMENTS

[0008]

Patent Document 1: JP 2008-260927 A

Patent Document 2: JP 2006-330209 A

Patent Document 3: JP 2010-102086 A

Patent Document 4: WO 2008/065944

Patent Document 5: WO 2009/096050

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0009]

In view of the above-described drawbacks of the prior art, an object of the present invention is to provide a colored resin composition with which a black matrix having a high adhesion with a substrate surface constituted by a metal or an inorganic material, and having a high chemical resistance can be readily formed. Through the use of such a colored resin composition, a resin black matrix and a substrate for touch panel having excellent reliability can be obtained.

MEANS FOR SOLVING THE PROBLEMS

[0010]

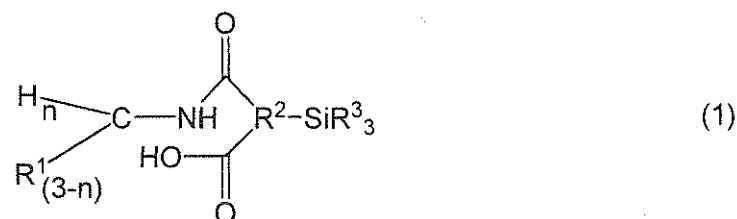
To solve the problems of the prior art, the present inventors have intensively studied to discover that the problem to be solved by the present invention can be solved by using, as an adhesion promoter, a silane coupling agent having a specific structure.

[0011]

Thus, the object of the present invention is achieved by the following constitution:

(1) A colored resin composition comprising at least (A) a color pigment; (B) an alkali-soluble resin, (C) an adhesion promoter and (D) an organic solvent, the composition comprising as the (C) adhesion promoter at least a silane coupling agent represented by the Formula (1) below:

[0012]



[0013]

(wherein R^1 may be the same or different from each other and represents a $\text{C}_1\text{-C}_6$ alkyl group which optionally has a substituent(s); n represents 0 or 1; R^2 represents a $\text{C}_3\text{-C}_{30}$ trivalent organic group; R^3 may be the same or different from each other and represents a $\text{C}_1\text{-C}_6$ alkyl group, a $\text{C}_1\text{-C}_6$ alkoxy group, a phenyl group, a hydroxyl group or a phenoxy group wherein each of the groups other than the hydroxyl group optionally has a substituent(s)).

(2) The colored resin composition according to (1), wherein the (C) adhesion promoter is a silane coupling agent represented by the Formula (1) wherein $n = 0$.

(3) The colored resin composition according to (1) or (2), which comprises at least two silane coupling agents as the (C) adhesion promoter.

(4) The colored resin composition according to any one of (1) to (3), wherein the (A) color pigment is a black light-shielding material.

5 (5) The colored resin composition according to any one of (1) to (4), which comprises at least titanium nitride compound particles and/or carbon black as the black light-shielding material.

(6) The colored resin composition according to (5), wherein the weight ratio of the titanium nitride compound particles to the total weight of the black light-
10 shielding material is 20 to 80% by weight.

(7) A resin black matrix substrate obtained by applying the black resin composition according to any one of (4) to (6) onto a transparent substrate and forming a pattern.

EFFECTS OF THE INVENTION

15 [0014]

Through the use of the colored resin composition of the present invention, a resin black matrix having a high adhesion and a high chemical resistance can be easily obtained; and a black matrix substrate with excellent reliability can be obtained.

BEST MODE FOR CARRYING OUT THE INVENTION

20 [0015]

The present invention will now be described in more details.

[0016]

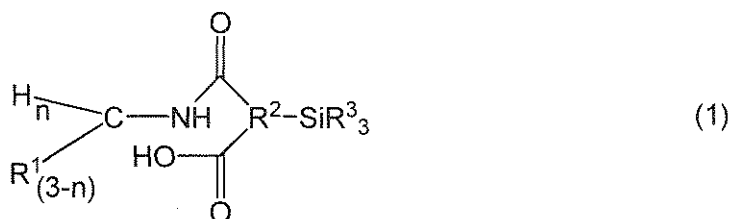
The colored resin composition according to the present invention comprises at least (A) a color pigment; (B) an alkali-soluble resin, (C) an adhesion promoter and
25 (D) an organic solvent. The composition comprises as the (C) adhesion promoter at least a silane coupling agent having a specific structure.

[0017]

The silane coupling agent has a structure represented by the Formula (1)

below:

[0018]



5 [0019]

(wherein R^1 may be the same or different from each other and represents a $\text{C}_1\text{-C}_6$ alkyl group. The alkyl group optionally has a substituent(s). n represents 0 or 1. R^2 represents a $\text{C}_3\text{-C}_{30}$ trivalent organic group. R^3 may be the same or different from each other and represents a $\text{C}_1\text{-C}_6$ alkyl group, a $\text{C}_1\text{-C}_6$ alkoxy group, a phenyl group, a hydroxyl group or a phenoxy group. Each of the groups other than the hydroxyl group optionally has a substituent(s)).

10 Here, R^1 is preferably methyl, ethyl, or butyl, and, in particular, methyl and ethyl are preferred because of raw material availability. R^1 may have a substituent(s) such as alkoxy, aryl, phenoxy, or halogen. R^2 is preferably a $\text{C}_3\text{-C}_{10}$ trivalent organic group in view of the solubility in organic solvents.

[0020]

Examples of the silane coupling agent of the present invention represented by Formula (1) include 3-(*tert*-butylcarbamoyl)-6-(trimethoxysilyl) hexanoic acid, 2-(2-(*tert*-butylamino)-2-oxoethyl)-5-(trimethoxysilyl) pentane acid, 3-(isopropylcarbamoyl)-6-(trimethoxysilyl) hexanoic acid, 2-(2-(isopropylamino)-2-oxoethyl)-5-(trimethoxysilyl) pentane acid, 3-(isobutylcarbamoyl)-6-(trimethoxysilyl) hexanoic acid, 2-(2-(isobutylamino)-2-oxoethyl)-5-(trimethoxysilyl) pentane acid, 3-(*tert*-pentylcarbamoyl)-6-(trimethoxysilyl) hexanoic acid, 2-(2-(*tert*-pentylamino)-2-oxoethyl)-5-(trimethoxysilyl) pentane acid, 3-(*tert*-butylcarbamoyl)-6-(triethoxysilyl)

hexanoic acid, 2-(2-(*tert*-butylamino)-2-oxoethyl)-5-(triethoxysilyl) pentane acid, 6-(dimethoxy(methyl)silyl)-3-(*tert*-butylcarbamoyl) hexanoic acid, 5-(dimethoxy(methyl)silyl)-2-(2-(*tert*-butylamino)-2-oxoethyl) pentane acid, 3-(*tert*-butylcarbamoyl)-6-(trimethoxysilyl) pentane acid, 2-(2-(*tert*-butylamino)-2-oxoethyl)-5-(trimethoxysilyl) butanoic acid, 2-(*tert*-butylcarbamoyl)-4-(2-(trimethoxysilyl)ethyl)cyclohexane carboxylic acid, 2-(*tert*-butylcarbamoyl)-5-(2-(trimethoxysilyl)ethyl)cyclohexane carboxylic acid, and the like.

[0021]

Among these, the compounds of Formula (1) above wherein $n = 0$ are preferred the effect of improving adhesion to soda glass or ITO is promoted.

[0022]

Specifically, 3-(*tert*-butylcarbamoyl)-6-(trimethoxysilyl) hexanoic acid, 2-(2-(*tert*-butylamino)-2-oxoethyl)-5-(trimethoxysilyl) pentane acid, 3-(isopropylcarbamoyl)-6-(trimethoxysilyl) hexanoic acid, 3-(*tert*-pentylcarbamoyl)-6-(trimethoxysilyl) hexanoic acid, 2-(2-(*tert*-pentylamino)-2-oxoethyl)-5-(trimethoxysilyl) pentane acid, 3-(*tert*-butylcarbamoyl)-6-(triethoxysilyl) hexanoic acid, 2-(2-(*tert*-butylamino)-2-oxoethyl)-5-(triethoxysilyl) pentane acid, 6-(dimethoxy(methyl)silyl)-3-(*tert*-butylcarbamoyl) hexanoic acid, 5-(dimethoxy(methyl)silyl)-2-(2-(*tert*-butylamino)-2-oxoethyl) pentane acid, 3-(*tert*-butylcarbamoyl)-6-(trimethoxysilyl) pentane acid, 2-(2-(*tert*-butylamino)-2-oxoethyl)-5-(trimethoxysilyl) butanoic acid, 2-(*tert*-butylcarbamoyl)-4-(2-(trimethoxysilyl)ethyl)cyclohexanehexane carboxylic acid, and 2-(*tert*-butylcarbamoyl)-5-(2-(trimethoxysilyl)ethyl)cyclohexanehexane carboxylic acid are included.

[0023]

When the silane coupling agent having the above-described specific structure is added as the (C) adhesion promoter to the colored resin composition, although it

may be added individually, it is preferred to co-use a known silane coupling agent.

Although promotion of the adhesion with the underlying substrate and of the chemical resistance of the coating can be attained by increasing the amount of the above-described silane coupling agent added, a problem, for example, in that the fine patterns are lost during development with an alkali so that the resolution is decreased is likely to occur. Therefore, in view of promoting the adhesion with the underlying material during the development, it is preferred to use two or more silane coupling agents in combination.

[0024]

The silane coupling agents to be mixed and used in combination are not restricted and include, but are not limited to, silane coupling agents having a functional group(s) such as vinyl group(s), epoxy group(s), styryl group(s), methacryloxy group(s), acryloxy group(s) and amino group(s). Preferred specific examples include 3-glycidoxypropyltrimethoxysilane, 3-glycidoxypropyltriethoxysilane, 3-glycidoxypropylmethyldimethoxysilane, 3-glycidoxypropylmethyldiethoxysilane, 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, 3-chloropropylmethyldimethoxysilane, 3-chloropropyltrimethoxysilane, vinyltrimethoxysilane, vinyltriethoxysilane, vinyltris(2-methoxyethoxy)silane, *N*-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane, *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane, 3-methacryloxypropyltrimethoxysilane, 3-acryloxypropyltrimethoxysilane, 3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, 3-triethoxysilyl-*N*-(1,3-dimethylbutylidene)propylamine, 3-mercaptopropyltrimethoxysilane, 3-ureidopropyltriethoxysilane, 3-isocyanatepropyltriethoxysilane and *p*-styryltrimethoxysilane.

[0025]

As a method of preparing these silane coupling agents, a preparation method

by the reaction of a silane coupling agent containing an acid anhydride and an alkyl amine is preferred in view of ease of preparation. In this case, depending on the structure of the silane coupling agent containing an acid anhydride, two types of silane coupling agent generate at the same time. However, they can be used as a mixture without separation or purification. Further, although this synthesis method can possibly cause side production of, for example, a small amount of oligomers, this does not significantly affect the adhesion-promoting effect and need not be considered.

[0026]

The amount to be added is preferably 1 to 15% by weight, more preferably 2 to 10% by weight based on the total amount of the solid components in the colored resin composition, that is, the total of the (A) color pigment and the (B) alkali-soluble resin. If it is less than 1% by weight, the adhesion-promoting effect is not sufficient, and if it is more than 15% by weight, fine patterns are lost in the development with an alkali, so that the resolution is decreased.

[0027]

The black resin composition of the present invention can be used to produce printing inks, ink jet inks, materials for photomask production, materials for proof printing production, etching resists, solder resists, bulkheads of plasma display panel (PDP), dielectric patterns, electrode (conductor circuit) patterns, circuit patterns of electronic components, conductive pastes, conductive films, light-shielding images such as black matrix, and the like. Preferably, the black resin composition can be advantageously employed to set a light-shielding image (including black matrix), e.g., in a gap of a coloring pattern, vicinity portions, and in the side of the outside light of TFT to improve the display property of color filters for color liquid crystal displays and the like, and can be advantageously employed for light-shielding films for touch panels.

[0028]

Especially preferably, the composition is used in liquid crystal displays, plasma displays, EL displays equipped with inorganic EL, CRT displays, and displays comprising a touch panel, as a black matrix such as black edges formed on the peripheral portion, lattice- or stripe-like black portions between color pixels of red, blue, and green, and, more preferably, as a black matrix formed in color filters for liquid crystal displays and as a black matrix formed on cover glass for touch panels.

[0029]

The black matrix formed on the cover glass of a touch panel plays a role as a frame which shields the light leaked from the LCD panel. To improve the design, the frame may be formed with a colored matrix made from a colored resin composition other than black. The colored resin composition of the present invention can suitably be used therefor.

[0030]

As the (A) color pigment in the colored composition of the present invention, either an organic pigment or an inorganic pigment can suitably be used. Among the pigments, those having a good adhesion and excellent light resistance, heat resistance and chemical resistance are especially preferred. Representative examples of the pigments expressed in terms of color index (CI) number include, but are not limited to, the following:

[0031]

Examples of red pigments include Pigment Red (hereinafter referred to as "PR") 9, PR48, PR97, PR122, PR123, PR144, PR149, PR166, PR168, PR177, PR179, PR180, PR192, PR209, PR215, PR216, PR217, PR220, PR223, PR224, PR226, PR227, PR228, PR240, PR254 and the like.

[0032]

Examples of orange pigments include Pigment Orange (hereinafter referred to as "PO" for short) 13, PO36, PO38, PO43, PO51, PO55, PO59, PO61, PO64, PO65, PO71 and the like.

[0033]

5 Examples of yellow pigments include Pigment Yellow (hereinafter referred to as "PY" for short) 12, PY13, PY17, PY20, PY24, PY83, PY86, PY93, PY95, PY109, PY110, PY117, PY125, PY129, PY137, PY138, PY139, PY147, PY148, PY150, PY153, PY154, PY166, PY168, PY185 and the like.

[0034]

10 Examples of violet pigments include Pigment Violet (hereinafter referred to as "PV" for short) 19, PV23, PV29, PV30, PV32, PV37, PV40, PV50 and the like.

[0035]

Examples of blue pigments include Pigment Blue (hereinafter referred to as "PB" for short) 15, PB15:3, PB15:4, PB15:6, PB22, PB60, PB64 and the like.

15 [0036]

Examples of green pigments include Pigment Green (hereinafter referred to as "PG" for short) 7, PG10, PG36, PG58 and the like.

[0037]

20 Examples of black pigments include black organic pigments, mixed color organic pigments, inorganic pigments and the like. Examples of the black organic pigments include carbon black, perylene black, aniline black and the like. Examples of the mixed color pigments include those made into pseudo-black by mixing two or more pigments selected from red, blue, green, violet, yellow, magenta, cyan and the like. Examples of the inorganic pigments include graphite; metal

25 particles such as titanium, copper, iron, manganese, cobalt, chromium, nickel, zinc, calcium, silver and the like; metal oxides; composite oxides; metal sulfides; metal nitrides; metal nitride oxides and the like. These may be used individually, or two

or more of these may be used in combination.

[0038]

Carbon black and titanium nitride compound are especially preferably used because of the high light-shielding performance.

5 [0039]

Examples of white pigments include titanium dioxide, barium carbonate, zirconium oxide, calcium carbonate, barium sulfate, alumina white, silicon dioxide and the like.

[0040]

10 The preferred characteristics of titanium nitride compound particles when used as the color pigment are described in detail below. "Titanium nitride compound" herein means one which contains titanium nitride as a major component, and usually contains titanium oxide TiO_2 , low-valent titanium oxide represented by $\text{Ti}_n\text{O}_{2n-1}$ ($1 \leq n \leq 20$) and titanium nitride oxide represented by TiN_xO_y ($0 < x < 2.0$,
15 $0.1 < y < 2.0$) as minor components.

[0041]

The angle of diffraction 2θ of the peak originated from (200) plane of the titanium nitride compound used in the present invention when $\text{CuK}\alpha$ radiation is used as the X-ray source is preferably 42.5° to 43.2° , more preferably 42.5° to 42.8° ,
20 still more preferably 42.5° to 42.7° . By using titanium nitride compound particles whose angle of diffraction 2θ is within this range, a high OD value can be attained while retaining a low concentration of the light-shielding material in the black resin composition. Further, since the composition has a high UV transmittance, a resin black matrix having a high precision and a good taper shape can be easily formed.

25 [0042]

As for the X-ray diffraction spectrum of the titanium compound when $\text{CuK}\alpha$ radiation is used as the X-ray source, as the peak with the strongest intensity, the

angle of diffraction 2θ of the peak originated from (200) plane of TiN is seen in the vicinity of $2\theta = 42.5^\circ$ whereas the angle of diffraction 2θ of the peak originated from (200) plane of TiO is seen in the vicinity of $2\theta = 43.4^\circ$. On the other hand, although the peaks are not the ones with the strongest intensity, the angle of diffraction 2θ of the peak originated from (200) plane of anatase-type TiO_2 is observed in the vicinity of $2\theta = 48.1^\circ$ whereas the angle of diffraction 2θ of the peak originated from (200) plane of rutile-type TiO_2 is observed in the vicinity of $2\theta = 39.2^\circ$. Thus, in the titanium compound with a crystal structure having nitrogen atoms and oxygen atoms, the peak with the strongest intensity is seen within the range where the angle of diffraction 2θ is from 42.5° to 43.4° . As the content of oxygen atoms in the crystal state increases, the peak position shifts to higher angle side compared to 42.5° . In the titanium nitride oxide in which the reduction by nitridation is insufficient obtained by nitriding titanium oxide, the peak with the strongest peak is observed at the angle of diffraction 2θ of 42.9° to 43.2° (JP 2006-209102 A).

[0043]

When titanium oxide TiO_2 is contained as a minor component, as the peak with the strongest intensity, the angle of diffraction 2θ of the peak originated from anatase-type TiO_2 (101) is seen in the vicinity of $2\theta = 25.3^\circ$ whereas the angle of diffraction 2θ of the peak originated from rutile-type TiO_2 (110) is seen in the vicinity of $2\theta = 27.4^\circ$. Yet, since TiO_2 is white and could be thus a factor which deteriorates the light-shielding performance, it is preferred that TiO_2 be decreased to the extent where it is not observed as the peak.

[0044]

The crystallite size can be determined from the half bandwidth of the X-ray diffraction peak according to the Scherrer's formula shown in the equations below (1) and (2).

[0045]

$$\text{Crystallite size (nm)} = \frac{K\lambda}{\beta \cos \theta} \quad (2)$$

[0046]

$$\beta = \sqrt{\beta_i^2 - \beta_o^2} \quad (3)$$

[0047]

5 In the formula, $K = 0.9$, λ = wavelength of X ray (0.15418 nm), β_e : half bandwidth of the diffraction peak, β_o : corrected value of the half bandwidth (0.12°), wherein β , β_e , and β_o are calculated in radians.

[0048]

10 The crystallite size is preferably not less than 10 nm, more preferably 10 to 50 nm, still more preferably 10 to 30 nm. If titanium nitride compound particles having a crystallite size is less than 10 nm, problems in that the light-shielding performance is deteriorated and the dispersability is decreased occur. On the other hand, when the crystallite size is more than 50 nm, problems in that the light-shielding performance is deteriorated and the particles likely to precipitate so that
15 shelf stability is decreased occur. In the present invention, it is preferred that the crystallite size be appropriately small because the reflection is close to colorless, even though the light-shielding performance is deteriorated when the crystallite is small.

[0049]

20 The specific surface area of the titanium nitride compound particles used in the present invention can be determined by BET method and is preferably 5 to 100 m²/g, more preferably 10 to 100 m²/g, still more preferably 30 to 100 m²/g. Based on the specific surface area determined by BET method when the particles are assumed to be completely spherical and have a uniform particle size, the particle size can be calculated by the equation (4) below.

25 [0050]

$$\text{BET average particle size (nm)} = 6/(S \times d \times 1000) \quad (4)$$

wherein S: specific surface area (m^2/g); d: density (g/cm^3); and $d = 5.24$ (g/cm^3) in case of titanium nitride, $d = 4.3$ (g/cm^3) in case of titanium nitride oxide [0051]

5 When the particles have a small specific surface area, i.e., a large primary particle size, it is difficult to disperse the particles finely, and problems arise in that the particles precipitate during storage; the flatness decreases when used as a resin black matrix; and the adhesion to glass decreases. When the particles have a large specific surface area, i.e., a small primary particle size, the particles are easily
10 aggregated when dispersed, and, consequently, problems arise in that the dispersion stability tends to be worse, and when used as a resin black matrix, a sufficient hiding power of light-shielding material may not be provided and the OD value decreases, which is not preferred.

[0052]

15 A primary particle can be said to be an aggregate of a number of crystallites but is preferably constituted by uniform crystallites. In other words, the relationship between the crystallite size determined from the half bandwidth of X-ray diffraction peak and the particle size determined from the specific surface area preferably satisfies the expression (5) below.

20 [0053]

$$\text{BET average particle size (nm)} < \text{crystallite size (nm)} \times 2 \quad (5)$$

The titanium nitride compound particles used in the present invention contain TiN as a major component, and generally contain some oxygen atoms resulting from, for example, contamination of oxygen during synthesis and oxidation of the particle
25 surface, which is especially marked when the particle size is small. The less oxygen content is preferred because a higher OD value can be obtained, and, in particular, it is preferable not to contain TiO_2 as a minor component. However, the less the

oxygen content is, the more reddish the reflected color becomes, and thus the particles preferably contain oxygen atoms moderately. The content of oxygen atoms is preferably 5% by weight to 20% by weight, and more preferably 8% by weight to 20% by weight.

5 [0054]

The content of titanium atoms can be analyzed by ICP optical emission spectrometry. The content of nitrogen atoms can be analyzed by inert gas fusion-thermal conductivity method. The content of oxygen atoms can be analyzed by inert gas fusion-infrared absorption method.

10 [0055]

For synthesizing a titanium nitride, a gas-phase reaction method is generally used. Examples of the method include electric furnace process and thermal plasma method, and the thermal plasma method is preferred because the method causes less contamination of impurities, allows synthesis of particles with a uniform size, and shows high productivity. Specifically, the primary particle of the titanium nitride compound synthesized by the thermal plasma method is formed of substantially uniform crystallites, and using the titanium nitride compound synthesized by the thermal plasma method allows formation of a black matrix having a lower dielectric constant, which is preferred.

20 [0056]

Examples of methods for generating thermal plasma include DC arc-discharge, multiple-phase arc-discharge, high-frequency (RF) plasma, and hybrid plasma, among which the high frequency plasma which causes less impurity contamination from an electrode is more preferred. Specific examples of methods for producing titanium nitride compound particles by the thermal plasma method include, but are not limited to, reacting titanium tetrachloride with ammonium gas in a plasma flame (JP 02-22110 A), synthesis by vaporizing titanium powders with

high-frequency thermal plasma and nitriding with nitrogen introduced as a carrier gas in a cooling process (JP 61-11140 A), and passing ammonia gas through the peripheral portion of plasma (JP 63-85007 A). Any production method may be employed as long as it produces titanium nitride compound particles having desired properties. Various types of titanium nitride compound particles are commercially available, and a number of titanium nitride compound particles satisfying the angle of diffraction and the amount of oxygen atoms defined in the present invention, and, furthermore, the preferred particle size and specific surface area described above are also commercially available. Such commercially available products may be preferably used in the present invention.

[0057]

Preferred characteristics of carbon black when used in the present invention are now described in detail.

[0058]

As the carbon black used in the present invention, it is preferable to use a carbon black having insulation properties improved by surface treatment. Examples of commonly known treatments to improve insulation properties include surface coating with resin (JP 2002-249678 A), wet surface-oxidation treatment (JP 4464081 B), and surface modification with an organic group comprising a non-polymeric group (JP 2008-517330 A)). In the present invention, it is preferable to use a carbon black that is surface-modified with an organic group comprising a non-polymeric group, and through the use of such a carbon black, a resin black matrix that has high insulation properties even after high-temperature heat treatment can be obtained. In particular, it is preferable to use a carbon black that is surface-modified with an organic group having a sulfonic acid group, because high insulation properties can be achieved and reduction in insulation properties due to high-temperature treatment can be prevented.

[0059]

For the surface composition of the carbon black in the present invention, it is necessary that the percentage of carbon atoms be 95% or less, and the percentage of sulfur atoms 0.5% or more. Further, it is preferred that the percentage of carbon atoms be 95% or less, and the percentage of sulfur atoms 1.0% or more. It is more preferred that the percentage of carbon atoms be 90% or less, and the percentage of sulfur atoms 1.0% or more. The higher the percentage of sulfur atoms on the carbon black surface is, the more effectively a binder resin is adsorbed to the carbon black, and the resulting steric hindrance prevents contact between carbon blacks, leading to improved insulation properties of a resin black matrix.

[0060]

The sulfur components present at the surface of the carbon black is present in the form of disulfide, carbon disulfide, and oxide, and to make the effects of the present invention prominent, the sulfur components are desirably present in the form of oxide. Specifically, it is desirably present in the form of SO and SO_x ($2 \leq x \leq 4$). The state of S atoms on the carbon black surface can be determined by X-ray photoelectron spectroscopy (XPS), and their abundance ratio can be determined by classifying S2p peak components into components assigned to C-S and S-S and components assigned to SO and SO_x ($2 \leq x \leq 4$).

[0061]

In the sulfur components present at the surface of the carbon black in the present invention, the percentage of components derived from SO and SO_x is preferably 70% or more, and more preferably 80% or more. The higher the percentage of components derived from SO and SO_x in the sulfur components present at the surface is, the higher the insulation properties become, and, further, the less the reduction in insulation properties due to high-temperature treatment is, which is preferred. The mechanism why a large amount of components derived from SO

and SOx provides higher insulation properties and thermal stability is not clear, but is presumably because the adsorption of a binder resin to the carbon black becomes stronger. A similar analysis of the surface state of a surface-oxidized carbon black that is conventionally used shows that the percentage of components derived from SO and SOx in sulfur components present at the surface is 70% or less, and it can be said that the surface state is completely different.

[0062]

The specific surface area of the carbon black used in the present invention is not restricted, and the value measured by the BET method using nitrogen adsorption is preferably 10 m²/g to 600 m²/g, more preferably 20 m²/g to 200 m²/g, and still more preferably 20 m²/g to 100 m²/g. When the carbon black has a large specific surface area, i.e., a small primary particle size, the particles are easily aggregated, and, therefore, it is difficult to stabilize dispersion, which leads to deteriorated storage stability. When the carbon black has a small specific surface area, i.e., a large primary particle size, the light-shielding effect decreases, or carbon blacks come in contact with each other in a resin coating to reduce the insulation properties of the black resin coating, which is not preferred.

[0063]

To make the effects of the present invention prominent, it is preferred to use titanium nitride compound and/or carbon black as the (A) color pigment. The percentage of the titanium nitride compound in the total weight of the light-shielding material (A) is preferably 20 to 80% by weight, and more preferably 30 to 70% by weight. When the percentage of the titanium nitride compound is small, the reflected hue has an achromatic color, but the insulation properties are reduced, which is not preferred. In particular, reduction in insulation properties due to high-temperature thermal history will be significant, and, further, the dielectric constant will be high, which is not preferred. The larger the percentage of the titanium

nitride compound is, the higher the insulation properties and light-shielding effect are, but the more reddish the reflected hue is. Therefore, the percentage of the titanium nitride compound is preferably within the range described above.

[0064]

5 In the present invention, the alkali-soluble resin (C) is an essential component, and any resin may be used as long as it acts as a binder to pigments and is soluble in alkaline developer in a developing process when forming a pattern such as a black matrix. Both photosensitive resins and non-photosensitive resins may be used, and, specifically, epoxy resins, acrylic resins, siloxane polymer-based resins, polyimide
10 resins, and the like are preferably used. In particular, acrylic resins or polyimide resins are suitably used because they are excellent, for example, in heat resistance of a coating and storage stability of the black resin composition. Further, photosensitive alkali-soluble resins are suitably used because, in forming a pattern such as a black matrix, using a photosensitive resin facilitates the pattern-forming
15 process.

[0065]

Examples of photosensitive alkali-soluble resins are shown below, but are not limited thereto.

[0066]

20 The photosensitive alkali-soluble resin is composed at least of an alkali-soluble polymer, a reactive monomer, and a photopolymerization initiator. For the quantitative ratio of them, the weight ratio of the alkali-soluble polymer to the reactive monomer is generally 10/90 to 90/10, and the amount of the photopolymerization initiator is about 1 to 20% by weight based on the total weight
25 the polymer and the monomer.

[0067]

As the alkali-soluble polymer, an alkali-soluble polymer having a carboxyl

group is preferred, and unsaturated carboxylic acid can preferably be used.

Examples of unsaturated carboxylic acids include monocarboxylic acids such as acrylic acid, methacrylic acid, crotonic acid, and vinyl acetic acid; dicarboxylic acids such as itaconic acid, maleic acid, and fumaric acid, or acid anhydrides thereof; and

5 polycarboxylic acid monoesters such as phthalic acid mono(2-

(meth)acryloyloxyethyl) ester. In particular, an acrylic polymer comprising a constituent unit derived from (meth)acrylic acid is preferred, and, further, an acrylic polymer obtained by reacting carboxylic acid contained in constituent units with a compound comprising an ethylenically unsaturated group and an epoxy group can

10 preferably be used because it improves the sensitivity in exposure and developing.

As the ethylenically unsaturated group, acrylic group and methacrylic group are preferred.

[0068]

These may be used alone or in combination with another copolymerizable

15 ethylenically unsaturated compound. Specific examples of copolymerizable ethylenically unsaturated compounds include, but are not limited to, unsaturated carboxylic acid alkyl esters such as methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, *n*-propyl acrylate, isopropyl acrylate, *n*-propyl

methacrylate, isopropyl methacrylate, *n*-butyl acrylate, *n*-butyl methacrylate, *sec*-

20 butyl acrylate, *sec*-butyl methacrylate, *iso*-butyl acrylate, *iso*-butyl methacrylate, *tert*-butyl acrylate, *tert*-butyl methacrylate, *n*-pentyl acrylate, *n*-pentyl methacrylate, 2-

hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, benzyl acrylate, and benzyl

methacrylate; aromatic vinyl compounds such as styrene, *p*-methylstyrene, *o*-

methylstyrene, *m*-methylstyrene, and α -methylstyrene; (cross-linked) cyclic

25 hydrocarbon groups such as tricyclodecanyl (meth)acrylate; unsaturated carboxylic

acid aminoalkyl esters such as aminoethyl acrylate; unsaturated carboxylic acid

glycidyl esters such as glycidyl acrylate and glycidyl methacrylate; carboxylic acid

vinyl esters such as vinyl acetate and vinyl propionate; vinyl cyanide compounds such as acrylonitrile, methacrylonitrile, and α -chloroacrylonitrile; aliphatic conjugated dienes such as 1,3-butadiene and isoprene; and polystyrene, polymethyl acrylate, polymethylmethacrylate, polybutylacrylate, and polybutylmethacrylate, each having an acryloyl group or a methacryloyl group at its terminal.

[0069]

In particular, an acrylic polymer comprising (meth)acrylic acid and benzyl (meth)acrylate is particularly preferred in view of dispersion stability and ease of patterning.

[0070]

When dispersing a pigment, adding the acrylic polymers described above in an amount of 5 to 50%, preferably 7 to 40%, based on the pigment provides a pigment dispersion in which the pigment is dispersed in a highly stable manner.

[0071]

Further, in addition to the above-described acrylic polymer obtained by reacting (meth)acrylic acid contained in constituent units with a compound comprising an ethylenically unsaturated group and an epoxy group, an acrylic polymer having an ethylenically unsaturated group in the side chain can preferably be used. Specific examples thereof include a copolymer described in JP 3120476 B and JP 08-262221 A, a photo-curing resin "Cyclomer (registered trademark) P" (Daicel Chemical Industries, Ltd.) which is a commercially available acrylic polymer, and an alkali-soluble cardo resin.

[0072]

The alkali-soluble polymer preferably has an average molecular weight (M_w) of 5,000 to 40,000 (measured by gel permeation chromatography using tetrahydrofuran as a carrier and calculated using a calibration curve of a standard polystyrene), and, further, a polymer having an average molecular weight of 8,000 to

40,000 and an acid value of 60 to 150 (mgKOH/g) is most preferred in view of photosensitive properties, solubility in ester solvents, solubility in alkaline developers, and prevention of residues.

[0073]

5 The reactive monomer may be a multifunctional/monofunctional acrylic monomer or oligomer. Examples of multifunctional monomers include bisphenol A diglycidyl ether (meth)acrylate, poly (meth)acrylatecarbamate, denatured bisphenol A epoxy (meth)acrylate, adipic acid 1,6-hexanediol (meth)acrylic ester, phthalic anhydride propylene oxide (meth)acrylic ester, trimellitic acid diethylene glycol (meth)acrylic ester, rosin-modified epoxydi(meth)acrylate, alkyd-modified (meth)acrylate, fluorene diacrylate-based oligomers described in Japanese Patent No. 3621533 or JP 08-278630 A, tripropylene glycol di(meth)acrylate, 1,6-hexane diol di(meth)acrylate, bisphenol A diglycidyl ether di(meth)acrylate, trimethylolpropane tri(meth)acrylate, pentaerythritol tri(meth)acrylate, triacrylformal, pentaerythritol 15 tetra(meth)acrylate and acid modifications thereof, dipentaerythritol hexa(meth)acrylate and acid modifications thereof, dipentaerythritol penta(meth)acrylate and acid modifications thereof, 2,2-bis[4-(3-acryloxy-2-hydroxypropoxy)phenyl]propane, bis[4-(3-acryloxy-2-hydroxypropoxy)phenyl]methane, bis[4-(3-acryloxy-2-hydroxypropoxy)phenyl]sulfone, bis[4-(3-acryloxy-2-hydroxypropoxy)phenyl]ether, 20 4,4'-bis[4-(3-acryloxy-2-hydroxypropoxy)phenyl]cyclohexane, 9,9-bis[4-(3-acryloxy-2-hydroxypropoxy)phenyl]fluorene, 9,9-bis[3-methyl-4-(3-acryloxy-2-hydroxypropoxy)phenyl]fluorene, 9,9-bis[3-chloro-4-(3-acryloxy-2-hydroxypropoxy)phenyl]fluorene, bisphenoxyethanol fluorene diacrylate, 25 bisphenoxyethanol fluorene dimethacrylate, bis cresol fluorene diacrylate, and bis cresol fluorene dimethacrylate. These may be used alone or in combination.

[0074]

Selection and combination of these polyfunctional monomers and oligomers enables control of resist sensitivity and workability. In particular, to increase the sensitivity, use of a compound having three or more functional groups, more preferably five or more functional groups, is preferred, and, in particular,

5 dipentaerythritol hexa(meth)acrylate, dipentaerythritol penta(meth)acrylate, and acid modifications thereof are preferred. Further, unsaturated group-containing alkali-soluble monomers obtained by reacting a reactant of an epoxy compound having two glycidyl ether groups and methacrylic acid with polybasic carboxylic acid or acid anhydride thereof are also preferably used in view of developability and workability.

10 Further, combined use with a (meth)acrylate containing a large number of aromatic rings and having a highly water-repellent fluorene ring in its molecule is preferred because a pattern can be controlled to a desired shape in development.

[0075]

The photopolymerization initiator is not restricted, and it preferably contains

15 an alkylphenone photopolymerization initiator and/or an oxime ester photopolymerization initiator.

[0076]

Examples of alkylphenone photopolymerization initiators include α -aminoalkylphenone photopolymerization initiators and α -hydroxyalkylphenone

20 photopolymerization initiators, and the α -aminoalkylphenone photopolymerization initiators are particularly preferred in view of high sensitivity. Examples thereof include 2,2-diethoxyacetophenone, 2-methyl-1-(4-methylthio phenyl)-2-morpholinopropan-1-one, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone ("Irgacure (registered trademark)" 369), 2-(dimethylamino)-2-[(4-

25 methylphenyl)methyl]-1-[4-(4-morpholinyl)phenyl]-1-butanone ("Irgacure (registered trademark)" 379), 1-hydroxycyclohexyl phenyl ketone, and 2-hydroxy-2-methyl-1-phenyl propan-1-one.

[0077]

Specific examples of oxime ester photopolymerization initiators include 1,2-octanedione, 1-[4-(phenylthio)-2-(O-benzoyloxime)] ("Irgacure (registered trademark)" OXE01), ethanone, 1-[9-ethyl-6-(2-methylbenzoyl)-9H-carbazol-3-yl]-, 1-(O-acetyloxime) ("Irgacure (registered trademark)" OXE02), and "ADEKA (registered trademark) OPTOMER" N-1818, N-1919, and "ADEKA ARKLS" NCI-831 available from Asahi Denka Kogyo K.K.

[0078]

In addition to these photopolymerization initiators, known photopolymerization initiators, e.g., inorganic photopolymerization initiators such as benzophenone compounds, thioxanthone compounds, imidazole compounds, benzothiazole compounds, benzooxazole compounds, carbazole compounds, triazine compounds, phosphorus compounds, or titanates can be used in combination. Examples thereof include benzophenone, N,N'-tetraethyl-4,4'-diaminobenzophenone, 4-methoxy-4'-dimethylaminobenzophenone, benzoin, benzoin methyl ether, benzoin isobutyl ether, benzyldimethylketal, α -hydroxyisobutylphenone, thioxanthone, 2-chlorothioxanthone, *t*-butylanthraquinone, 1-chloroanthraquinone, 2,3-dichloroanthraquinone, 3-chloro-2-methylanthraquinone, 2-ethylanthraquinone, 1,4-naphthoquinone, 9,10-phenanthraquinone, 1,2-benzoanthraquinone, 1,4-dimethylanthraquinone, 2-phenylanthraquinone, 2-(*o*-chlorophenyl)-4,5-diphenylimidazole dimer, 2-mercapto benzothiazole, 2-mercaptobenzooxazole, and 4-(*p*-methoxyphenyl)-2,6-di-(trichloromethyl)-s-triazine.

[0079]

The organic solvent (C) used for the black resin composition of the present invention is not restricted, and esters, aliphatic alcohols, ketones, and the like can be used.

[0080]

Specific examples of esters include, but are not limited to, benzyl acetate (boiling point: 214°C), ethyl benzoate (boiling point: 213°C), γ -butyrolactone (boiling point: 204°C), methyl benzoate (boiling point: 200°C), diethyl malonate (boiling point: 199°C), 2-ethylhexyl acetate (boiling point: 199°C), 2-butoxyethyl acetate (boiling point: 192°C), 3-methoxy-3-methyl-butyl acetate (boiling point: 188°C), diethyl oxalate (boiling point: 185°C), ethyl acetoacetate (boiling point: 181°C), cyclohexyl acetate (boiling point: 174°C), 3-methoxy-butyl acetate (boiling point: 173°C), methyl acetoacetate (boiling point: 172°C), ethyl-3-ethoxy propionate (boiling point: 170°C), 2-ethyl butyl acetate (boiling point: 162°C), isopentyl propionate (boiling point: 160°C), propylene glycol monomethyl ether propionate (boiling point: 160°C), propylene glycol monoethyl ether acetate (boiling point: 158°C), pentyl acetate (boiling point: 150°C), and propylene glycol monomethyl ether acetate (boiling point: 146°C).

[0081]

Among these solvents, acetic acid ester solvents or propionic acid ester solvents such as 3-methoxy-3-methyl-butyl acetate, propylene glycol monoethyl ether acetate, propylene glycol monomethyl ether propionate, 3-methoxy-butyl acetate, and propylene glycol monomethyl ether acetate are particularly preferred.

[0082]

Further, solvents other than the solvents described above, e.g., aliphatic ethers such as propylene glycol derivatives such as propylene glycol monomethyl ether (boiling point: 120°C), propylene glycol monoethyl ether (boiling point: 133°C), propylene glycol tertiary butyl ether (boiling point: 153°C), and dipropylene glycol monomethyl ether (boiling point: 188°C); aliphatic esters other than the above such as ethyl acetate (boiling point: 77°C), butyl acetate (boiling point: 126°C), and isopentyl acetate (boiling point: 142°C); aliphatic alcohols such as butanol (boiling point: 118°C), 3-methyl-2-butanol (boiling point: 112°C), and 3-methyl-3-

methoxybutanol (boiling point: 174°C); ketones such as cyclopentanone and cyclohexanone; solvents such as xylene (boiling point: 144°C), ethyl benzene (boiling point: 136°C), and solvent naphtha (petroleum fraction, boiling point: 165 to 178°C) can also be used in combination.

5 [0083]

Further, as the size of substrates increases, coating with a die coating apparatus is becoming predominant, so that the solvent is preferably a mixed solvent comprising two or more components in order to achieve an appropriate volatility and drying properties. In cases where the boiling points of all the solvents constituting
10 the mixed solvent are not higher than 150°C, many problems arise in that uniformity of film thickness cannot be attained; the film thickness after coating increases; and pigments aggregate at a nozzle part from where the coating solution is ejected through a slit, so that streaking occurs in the coated film. In cases where the mixed solvent contains many solvents having a boiling point not lower than 200°C, the
15 coated film surface becomes adhesive, and sticking occurs. Hence, a mixed solvent containing 30 to 75% by mass of a solvent having a boiling point of 150°C to 200°C is preferred.

[0084]

In the black resin composition of the present invention, to disperse the light-
20 shielding material uniformly and stably in a resin solution, it is preferable to add a pigment dispersant. Examples of pigment dispersants include polyester-based polymeric pigment dispersants, acrylic-based polymeric pigment dispersants, polyurethane-based polymeric pigment dispersants, polyallylamine-based polymeric dispersants, pigment derivatives, cationic surfactants, nonionic surfactants, anionic
25 surfactants, and carbodiimide-based pigment dispersants.

[0085]

These pigment dispersants are appropriately selected depending on the type of

pigment. Further, these pigment dispersants may be used alone or in combination of two or more thereof. Since these polymeric dispersants are not photosensitive, adding them in large amounts may deteriorate the photosensitivity of a color resist of interest, and it is desirable to add them in a proper amount taking into account dispersion stability and photosensitivity. Adding them in an amount of 1 to 50 (% by mass), more preferably 3 to 30 (% by mass), based on pigments produces the effect of achieving highly stabilized dispersion without deteriorating photosensitivity, which is more preferred.

[0086]

To the black resin composition of the present invention, a surfactant can be added for the purpose of providing coating properties and smoothness of a colored coated film and preventing Benard Cells. The amount of the surfactant is generally 0.001 to 10% by mass, preferably 0.01 to 1% by mass, based on pigments. When the amount is too small, the effect of providing coating properties and smoothness of a colored coated film and preventing Benard Cells is not produced, and when the amount is too large, physical properties of a coated film can be poor.

[0087]

Specific examples of surfactants include anionic surfactants such as ammonium lauryl sulfate and polyoxyethylene alkyl ether sulfate triethanolamine; cationic surfactants such as stearylamine acetate and lauryl trimethyl ammonium chloride; amphoteric surfactants such as lauryldimethylamine oxide and lauryl carboxymethyl hydroxyethyl imidazolium betaine; nonionic surfactants such as polyoxyethylene lauryl ether, polyoxyethylene stearyl ether, and sorbitan monostearate; silicone-base surfactants having polydimethylsiloxane or the like as the main skeleton; and fluorochemical surfactants. These are not limiting examples, and in the present invention, the surfactants can be used alone or in combination of two or more thereof.

[0088]

In the black composition of the present invention, the weight ratio of pigment component/resin component is preferably in the range of 80/20 to 40/60 in order to obtain a black coated film having a high OD value. The pigment component herein
5 refers to the total of the light-shielding material (A) and color pigments for adjusting chromaticity, and the resin component refers to the total of the alkali-soluble resin (B) composed of polymers, monomers, and the like, oligomers, and additives such as photopolymerization initiators and polymeric dispersants. If the amount of the resin component is too small, the black coated film has poor adhesion to a substrate, and if
10 the amount of the pigment component is too small, optical density per thickness (OD value/ μm) decreases, both of which are problematic.

[0089]

In the black resin composition of the present invention, the solids concentration, that is, the total of the resin component and the pigment component is
15 preferably 2% to 30%, and more preferably 5% to 20%, in view of coating properties and drying properties. Accordingly, the black composition of the present invention preferably consists essentially of a solvent, a resin component, and a pigment component, wherein the total amount of the resin component and the light-shielding material is preferably 2% to 30%, and more preferably 5% to ore 20%, with the
20 balance being the solvent. As described above, surfactants may be contained in the concentration described above.

[0090]

The black resin composition of the present invention is produced by a method such as a method in which pigments are dispersed directly in a resin solution using a
25 disperser, or a method in which pigments are dispersed in water or an organic solvent using a disperser to produce a pigment dispersion, which is then mixed with a resin solution. The method of dispersing pigments is not restricted, and various methods

including those using a ball mill, a sand grinder, a triple roll mill, and a high-speed impact mill may be used. In view of dispersion efficiency and finely dispersing performance, using a bead mill is preferred. As the bead mill, a co-ball mill, a basket mill, a pin mill, a DYNO mill, and the like can be employed. As the beads
5 for the bead mill, titania beads, zirconia beads, and zircon beads are preferably used.
[0091]

The diameter of the beads used for dispersion is preferably 0.01 mm to 5.0 mm, and more preferably 0.03 mm to 1.0 mm. In cases where the primary particle size of the pigments and the size of secondary particles formed by aggregation of the
10 primary particles are small, fine dispersion beads of 0.03 mm to 0.10 mm are preferably used. In this case, it is preferred that dispersion be carried out by using a bead mill having a centrifugal separator capable of separating the fine dispersion beads from a dispersion. In cases where pigments containing larger submicron particles are dispersed, dispersion beads with a size of 0.10 mm or more are
15 preferably used because sufficient grinding strength can be attained to disperse the pigments finely.
[0092]

An example of the method of producing a resin black matrix substrate using the black resin composition of the present invention with a die coating apparatus will
20 be described. Examples of substrates generally used include transparent substrates such as soda glass, alkali-free glass, and quartz glass, but are not limited thereto. Examples of the die coating apparatus include the sheet coating apparatus disclosed, for example, in Japanese Patent No. 3139358 and Japanese Patent No. 3139359. Using this apparatus, the black resin composition (coating solution) of the present
25 invention is ejected from a nozzle, and a substrate is moved, whereby the black resin composition can be applied onto the substrate. In this case, since a large number of substrates are coated in sheet form, a long-time operation results in that pigments

aggregate at the nozzle part from where the coating solution is ejected through a slit, which can be a coating defect to cause yield decrease.

[0093]

In this case, the coating defect is solved to increase the yield by incorporating the step of wiping the nozzle, an ejection port of the apparatus, with a solvent containing the above-described ester solvent having a boiling point of 150°C or higher in an amount of 40% by mass based on the total solvent. As described above, the black resin composition is applied onto a substrate, and then the solvent is removed, for example, by air-drying, vacuum drying, or heat drying to form a coated film of the black resin composition. In particular, by performing a vacuum drying step and additional heat drying with an oven or a hot plate, coating defects caused by convection are solved to increase the yield. The vacuum drying is preferably carried out at normal temperature to 100°C for 5 seconds to 10 minutes at a reduced pressure of 500 to 10 (Pa), more preferably at a reduced pressure in the range of 150 to 50 (Pa). The heat drying is preferably carried out using an oven, a hot plate, or the like at a temperature in the range of 50 to 120°C for 10 seconds to 30 minutes.

[0094]

Next, a mask is placed on the coated film, and ultraviolet rays are irradiated using exposure equipment. Then, developing is performed using an alkaline developing solution. It is preferable to use an alkaline developing solution containing 0.1 to 5% of a surfactant such as a nonionic surfactant because a better pattern can be obtained. Examples of alkaline substances used in the alkaline developing solution include, but are not limited to, inorganic alkalis such as sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium silicate, sodium metasilicate, and aqueous ammonia; and organic alkalis such as primary amines such as ethylamine and *n*-propylamine; secondary amines such as diethylamine and di-*n*-propylamine; tertiary amines such as triethylamine and

methyldiethylamine; tetraalkylammonium hydroxides such as tetramethylammonium hydroxide (TMAH); quarternary ammonium salts such as choline; alcohol amines such as triethanolamine, diethanolamine, monoethanolamine, dimethylaminoethanol, and diethylaminoethanol; and cyclic amines such as pyrrole, piperidine, 1,8-diazabicyclo[5,4,0]-7-undecene, 1,5-diazabicyclo[4,3,0]-5-nonane, and morpholine.

5 [0095]

The concentration of the alkaline substance is 0.01% by mass to 50% by mass, preferably 0.02% by mass to 10% by mass, and more preferably 0.02 to 1% by mass. Further, when the developing solution is an aqueous alkaline solution, water-soluble

10 organic solvents such as ethanol, γ -butyrolactone, dimethylformamide, and N-methyl-2-pyrrolidone may be appropriately added to the developing solution.

[0096]

Among these developing solutions, an aqueous developing solution of an aqueous alkaline solution is preferred in view of work environment and waste

15 developing solution disposal.

[0097]

Any development method such as immersion method, spray method, or paddle method may be used. After the development, washing with pure water or the like is performed.

20 [0098]

The resulting coating pattern of the black resin composition is then heat-treated (post-baked) for patterning. The heat treatment is generally carried out continuously or stepwise, for example, in air, in a nitrogen atmosphere, or in vacuum at a temperature of 150 to 300°C, preferably 180 to 250°C, for 0.25 to 5 hours.

25 [0099]

The optical density (OD value) of the resin black matrix thus obtained from the black resin composition of the present invention is preferably 2.5 or more per 1.0

μm of film thickness within the visible wavelength range between 380 and 700 nm, more preferably 3.0 or more, and still more preferably 4.0 or more. The OD value is measured using a multi channel photo detector (MCPD2000 manufactured by OTSUKA ELECTRONICS CO., LTD.) and calculated by the equation (6) below

[0100]

$$\text{OD value} = \log_{10} (I_0/I) \quad (6)$$

wherein, I_0 represents the intensity of incident light, and I represents the intensity of transmitted light.

[0101]

The reflected light chromaticity of the resin black matrix is measured on the transparent substrate surface, and the chromaticity values (a^* , b^*) calculated by the CIE $L^*a^*b^*$ color system using the reflectance spectrum for standard illuminant C according to the method of JIS-Z8729 are preferably both -2.0 to 2.0, and more preferably -1.0 to 1.0. If the chromaticity values (a^* , b^*) are less than -2.0, a problem arises in that the image reflected in the film surface looks bluish and greenish when looking at the resin black matrix through the transparent substrate, and if they are more than 2.0, a problem arises in that the image reflected in the film surface looks reddish and yellowish.

[0102]

The surface resistance value ρ_s ($\Omega/\square$) of the resin black matrix is preferably 10^{10} ($\Omega/\square$) or more, and more preferably 10^{12} ($\Omega/\square$) or more. The surface resistance value can be determined by making measurements by the method according to "JIS K 6911".

[0103]

The relative dielectric constant ϵ_r at 1 MHz of the resin black matrix is preferably 10 or less, more preferably 8 or less, and still more preferably 6 or less. When the relative dielectric constant of the resin black matrix is more than 10, an

non-uniform electric field in a touch panel can be caused, leading to reduced sensitivity of a sensor electrode. The relative dielectric constant of the resin black matrix is preferably as small as possible. The lower limit thereof is not limited, but generally not less than 2 at 1 MHz.

5 EXAMPLES

[0104]

The present invention will now be described in more detail using Examples and Comparative Examples, but the present invention is by no means limited to the following examples.

10 [0105]

<Evaluation Method>

[Surface Elemental Composition]

The surface elements of the carbon black were measured by X-ray photoelectron spectroscopy (XPS) using a measuring device ESCALAB 220iXL (trade name) under the following measurement conditions: excitation X-ray; monochromatic AlK α 1,2 radiation (1486.6 eV), X-ray diameter; 1 mm, and photoelectron take-off angle; 90°.

15 [0106]

[Specific surface area]

20 The specific surface area of the particles was measured using a high-performance automatic gas adsorption apparatus ("BELSORP" 36) manufactured by BEL Japan, Inc. After vacuum degassing at 100°C, the adsorption isotherm of N₂ gas at a temperature of liquid nitrogen (77 K) was measured and analyzed by BET method to determine the specific surface area. From the value of the specific surface area, a BET particle size was determined by using the equation (4) described above. In the calculation, the specific gravity: $d = 5.24 \text{ (g/cm}^3\text{)}$ was used for the titanium nitride compound particles, and the specific gravity: $d = 1.80 \text{ (g/cm}^3\text{)}$ was

25

used for the carbon black.

[0107]

[X-Ray Diffraction]

X-ray diffraction was measured by filling a powdered sample in an aluminum
5 standard sample holder by the wide-angle X-ray diffraction method (RU-200R
manufactured by Rigaku Corporation). Measurements were made under the
following conditions: X-ray source; CuK α radiation, output; 50 kV/200 mA, slit
system; 1°-1°-0.15 mm-0.45 mm, measurement step (2θ); 0.02°, and scan rate;
2°/min. The angle of diffraction at the peak derived from (200) plane observed
10 around $2\theta = 46^\circ$ was measured. Further, from the half bandwidth of the peak
derived from (200) plane, the size of crystallites constituting the particles was
calculated using Scherrer's formula of the equations (1) and (2) described above.

[0108]

[Composition Analysis]

15 The content of titanium atoms was measured by ICP optical emission
spectrometry (ICP optical emission spectrometer SPS3000 manufactured by Seiko
Instruments Inc.). The contents of oxygen atoms and nitrogen atoms were measured
with Oxygen/Nitrogen analyzer EMGA-620W/C manufactured by HORIBA Ltd.,
and determined by inert gas fusion-infrared absorption method for oxygen atoms and
20 by inert gas fusion-thermal conductivity method for nitrogen atoms.

[0109]

[Adhesion Test]

A resin black matrix having a film thickness of 1.0 μm was formed on a soda
glass, and the adhesion between the soda glass and the hardened film was evaluated
25 by the cross-cut peeling test by adhesion tape according to JIS K5400 8.5.2 (1990).
In the surface of the hardened film on the glass substrate, 11 parallel lines were
drawn at 1 mm intervals in the perpendicularly crossing longitudinal and transverse

directions, respectively, with a cutter knife such that the each line reached the glass plate to form 100 cross-cut squares each sizing 1 mm x 1 mm. A Cellophane adhesive tape (width 18 mm, adhesive force = 3.7 N/10 mm) was attached to the surface of the cross-cut surface of the hardened film, and rubbed with an eraser (which passed the test according to JIS S6050) to adhere the tape. Then an edge of the tape was gripped to hold the tape in the direction perpendicularly to the plate and the tape was instantaneously peeled off, followed by visually counting the number of the cross-cut squares remaining on the plate. The adhesion was evaluated based on the area of the peeled off cross-cut squares according to the following criteria:

- 5: peeled off area 0%
- 4: peeled off area 1 - < 5%
- 3: peeled off area 5 - < 15%
- 2: peeled off area 15 - < 35%
- 1: peeled off area 35 - < 65%
- 0: peeled off area 65 - 100%

Further, to evaluate the adhesion after a wet heat treatment, a black matrix substrate subjected to a PCT (Pressure Cooker Test) treatment was also tested for the adhesion in the same manner as described above. The conditions of the PCT treatment were: temperature 121°C, humidity 100%, 2 atm, 12 hours.

[0110]

[Chemical Resistance Test]

A resin black matrix having a film thickness of 1.0 μm was formed on a soda glass, and immersed in aqua regia and an organic alkali solution, respectively, followed by evaluation of the adhesion in the same manner as described above. The conditions of the treatment with aqua regia were 50°C for 5 minutes in a mixed solution of hydrochloric acid/nitric acid/distilled water = 25/3/72% by weight. The conditions of the treatment with the organic alkali solution were 80°C for 5 minutes

in a mixed solution of MEA (monoethanolamine)/BDG (butyldiglycol) = 30/70% by weight.

[0111]

[Resolution]

5 Using a line-and-space patterns mask having a line width to space ratio of 1:1, a resin black matrix having a film thickness of 1.0 μm was formed on a soda glass, and the width of the line in the mask pattern with which the smallest pattern was able to be formed was evaluated.

[0112]

10 [OD Value]

A resin black matrix having a film thickness of 1.0 μm was formed on soda glass, and the OD value was determined using a multi channel photo detector (manufactured by OTSUKA ELECTRONICS CO., LTD., MCPD2000) by the equation (6) mentioned above.

15 [0113]

[Surface Resistance]

A resin black matrix with a film thickness of 1.0 μm was formed on soda glass, and the surface resistivity ($\Omega/\square$) was measured using a high resistance meter (Hiresta UP manufactured by Mitsubishi Chemical Corporation).

20 [0114]

Also after the black matrix was heat-treated in an oven at 250°C for 30 minutes, the surface resistivity was measured in a similar manner.

[0115]

[Reflected Light Chromaticity]

25 A resin black matrix with a film thickness of 1.0 μm was formed on soda glass with a thickness of 1.1 mm, and the chromaticity of light reflected from the glass surface was measured using an UltraViolet-Vis-Near InfraRed

spectrophotometer (Shimadzu spectrophotometer UV-2500PC) (measurement conditions: measured wavelength range; 300 to 780 nm, sampling pitch; 1.0 nm, scan rate; low, and slit width; 2.0 nm).

[0116]

5 Synthesis Example 1: Synthesis of Silane Coupling Agent Mixed Solution (a-1)

To 200 g of propylene glycol monomethyl ether acetate, 41.97 g (160 mmol) of 3-(trimethoxysilyl)propylsuccinic anhydride and 11.70 g (160 mmol) of t-butylamine were added, and the resulting mixture was stirred for a while at room temperature and then stirred at 40°C for 2 hours. Thereafter, the mixture was
10 heated to 80°C and allowed to react for 6 hours. The obtained solution was diluted with propylene glycol monomethyl ether acetate to a solid concentration of 20% to obtain a mixed solution (a-1) of 3-(tert-butylcarbamoyl)-6-(trimethoxysilyl)hexanoic acid and 2-(2-(tert-butylamino)-2-oxoethyl)-5-(trimethoxysilyl)pentanoic acid.

[0117]

15 Synthesis Example 2: Synthesis of Silane Coupling Agent Mixed Solution (a-2)

To 200 g of propylene glycol monomethyl ether acetate, 41.97 g (160 mmol) of 3-(trimethoxysilyl)propylsuccinic anhydride and 9.45 g (160 mmol) of t-pentylamine were added, and the resulting mixture was stirred for a while at room temperature and then stirred at 40°C for 2 hours. Thereafter, the mixture was
20 heated to 80°C and allowed to react for 6 hours. The obtained solution was diluted with propylene glycol monomethyl ether acetate to a solid concentration of 20% to obtain a mixed solution (a-2) of 2-(2-(t-pentylamino)-2-oxoethyl)-5-(trimethoxysilyl)pentanoic acid and 3-(tert-pentylcarbamoyl)-6-(trimethoxysilyl)hexanoic acid.

25 [0118]

Synthesis Example 3: Synthesis of Silane Coupling Agent Mixed Solution (a-3)

To 200 g of propylene glycol monomethyl ether acetate, 41.97 g (160 mmol)

of 3-(trimethoxysilyl)propylsuccinic anhydride and 9.45 g (160 mmol) of isopropylamine were added, and the resulting mixture was stirred for a while at room temperature and then stirred at 40°C for 2 hours. Thereafter, the mixture was heated to 80°C and allowed to react for 6 hours. The obtained solution was diluted with propylene glycol monomethyl ether acetate to a solid concentration of 20% to obtain a mixed solution (a-3) of 2-(2-(isopropylamino)-2-oxoethyl)-5-(trimethoxysilyl)pentanoic acid and 3-(tert-isopropylcarbamoyl)-6-(trimethoxysilyl)hexanoic acid.

[0119]

Synthesis Example 4: Synthesis of Silane Coupling Agent Mixed Solution (a-4)

To 200 g of propylene glycol monomethyl ether acetate, 41.97 g (160 mmol) of 3-(trimethoxysilyl)propylsuccinic anhydride and 9.45 g (160 mmol) of n-propylamine were added, and the resulting mixture was stirred for a while at room temperature and then stirred at 40°C for 2 hours. Thereafter, the mixture was heated to 80°C and allowed to react for 6 hours. The obtained solution was diluted with propylene glycol monomethyl ether acetate to a solid concentration of 20% to obtain a mixed solution (a-4) of 2-(2-oxo-2-(propylamino)ethyl)-5-(trimethoxysilyl)pentanoic acid and 3-(propylcarbamoyl)-6-(trimethoxysilyl)hexanoic acid.

[0120]

Synthesis Example 5: Synthesis of Silane Coupling Agent Mixed Solution (a-5)

To 200 g of propylene glycol monomethyl ether acetate, 41.97 g (160 mmol) of 3-(trimethoxysilyl)propylsuccinic anhydride and 14.90 g (160 mmol) of aniline were added, and the resulting mixture was stirred for a while at room temperature and then stirred at 40°C for 2 hours. Thereafter, the mixture was heated to 80°C and allowed to react for 6 hours. The obtained solution was diluted with propylene glycol monomethyl ether acetate to a solid concentration of 20% to obtain a mixed

solution (a-5) of 2-(2-oxo-2-(phenylamino)ethyl)-5-(trimethoxysilyl)pentanoic acid and 3-(phenylcarbamoyl)-6-(trimethoxysilyl)hexanoic acid.

[0121]

Synthesis Example 6: Synthesis of Silane Coupling Agent Mixed Solution (a-6)

5 To 200 g of propylene glycol monomethyl ether acetate, 41.97 g (160 mmol) of 3-(trimethoxysilyl)propylsuccinic anhydride and 7.37 g (160 mmol) of ethanol were added, and the resulting mixture was stirred for a while at room temperature and then stirred at 40°C for 2 hours. Thereafter, the mixture was heated to 80°C and allowed to react for 6 hours. The obtained solution was diluted with propylene
10 glycol monomethyl ether acetate to a solid concentration of 20% to obtain a mixed solution (a-6) of 4-ethoxy-4-oxo-2-(trimethoxysilyl)butanoic acid and 4-ethoxy-4-oxo-3-(trimethoxysilyl)butanoic acid.

[0122]

Synthesis Example 7: Synthesis of Silane Coupling Agent Solution (a-7)

15 To 400 g of propylene glycol monomethyl ether acetate, 41.97 g (160 mmol) of 3-(trimethoxysilyl)propylsuccinic anhydride and 11.70 g (160 mmol) of t-butylamine were added, and the resulting mixture was stirred for a while at room temperature, and then stirred at 60°C for 2 hours. Thereafter, the mixture was heated to 140°C and allowed to react for 6 hours under azeotropic distillation of
20 propylene glycol monomethyl ether acetate and water. The obtained solution was diluted with propylene glycol monomethyl ether acetate to a solid concentration of 20% to obtain a solution (a-7) of 1-(tert-butyl)-3-trimethoxysilylpyrrolidine-2,5-dione.

[0123]

Synthesis Example 8: Synthesis of Acrylic Polymer (P-1)

25 Methyl methacrylate/methacrylic acid/styrene copolymer (weight ratio: 30/40/30) was synthesized according to the method described in Example 1 of Japanese Patent No. 3120476, and then 40 parts by weight of glycidyl methacrylate

was added thereto. The resulting mixture was redeposited with purified water, filtered, and dried to obtain an acryl polymer (P-1) powder having an average molecular weight (Mw) of 15,000 and an acid value of 110 (mg KOH/g).

[0124]

5 Production Example 1: Production of Caron Black Dispersion (CB-1)

The surface elemental composition of a carbon black (CB-Bk1) which surface was modified with sulfonic acid groups by the method according to JP-A-2008-517330 was C: 88%, O: 7%, Na: 3% and S: 2%; as for the state of S element, the ratio of components assigned to C-S and S-S based on S2p peak components was
10 90%, and the ratio of components assigned to SO and SOx based on S2p peak components was 10%; and the BET value was 54 m²/g.

[0125]

The carbon black CB-Bk1 (200 g), a 40% by weight solution (94 g) of the acryl polymer (P-1) in propylene glycol monomethyl ether acetate, a 40% by weight
15 solution (31 g) of LPN 21116 available from by BYK Japan KK as a polymeric dispersant, and propylene glycol monomethyl ether acetate (675 g) were charged into a tank, and stirred with a homomixer (manufactured by Tokusyu Kika Kogyo Co., Ltd.) for 1 hour to obtain a pre-dispersion. Thereafter, the pre-dispersion was supplied to Ultra Apex Mill (manufactured by KOTOBUKI INDUSTRIES CO.,
20 LTD.) equipped with a centrifugation separator 70% filled with zirconia beads with a diameter of 0.05 mm (available from Nikkato Corporation, YTZ balls), and dispersion was carried out at a rotation speed of 8 m/s for 2 hours to obtain a carbon black dispersion CB-1 with a solids concentration of 25% by weight and pigment/resin (weight ratio) = 80/20.

25 [0126]

Production Example 2: Production of Titanium Black Dispersion (TB-1)

The angle of diffraction 2θ of the peak originated from the (200) plane of

titanium nitride compound particles produced by thermal plasma method (Ti-BK1, available from NISSHIN ENGINEERING INC., TiN UFP Lot 1320910202) was 42.62°; the crystallite size determined from half bandwidth of the peak was 21.9 nm; and the BET specific surface area was 85.0 m²/g. A composition analysis revealed that the content of titanium was 70.4% by weight; the content of nitrogen was 19.9% by weight; and the content of oxygen was 8.86% by weight. No X-ray diffraction peaks originated from TiO₂ were observed at all.

[0127]

The titanium nitride Ti-Bk1 (200 g), a 40% by weight solution of the acryl polymer (P-1) in propylene glycol monomethyl ether acetate (94 g), a 40% by weight solution (31 g) of LPN 21116 available from BYK Japan KK as a polymeric dispersant, and propylene glycol monomethyl ether acetate (675 g) were charged into a tank, and stirred with a homomixer (manufactured by Tokusyu Kika Kogyo Co., Ltd.) for 1 hour to obtain a pre-dispersion 1. Thereafter, the pre-dispersion 1 was supplied to Ultra Apex Mill (manufactured by KOTOBUKI INDUSTRIES CO., LTD.) equipped with a centrifugation separator 70% filled with zirconia beads with a diameter of 0.05 mm (available from Nikkato Corporation, YTZ balls), and dispersion was carried out at a rotation speed of 8 m/s for 2 hours to obtain a titanium black dispersion TB-1 with a solids concentration of 25% by weight and pigment/resin (weight ratio) = 80/20.

[0128]

Production Example 3: Production of Red Pigment Dispersion (R-1)

The organic pigment PY254 (R-1, produced by BASF) in an amount of 120 g, 100 g of a 40% by weight solution of the acryl polymer (P-1) in propylene glycol monoethyl ether acetate, 100 g of a 40% by weight solution of LPN 21116 available from BYK Japan KK as a polymeric dispersant, and 680 g of propylene glycol monoethyl ether acetate were charged into a tank, and stirred with a homomixer

(manufactured by PRIMIX Corporation) for 20 minutes to obtain a pre-dispersion. Thereafter, the pre-dispersion was supplied to Ultra Apex Mill (manufactured by KOTOBUKI INDUSTRIES CO., LTD.) equipped with a centrifugation separator 75% filled with zirconia beads with a diameter of 0.05 mm (available from Neturen Co., Ltd., YTZ balls), and dispersion was carried out at a rotation speed of 8 m/s for 3 hours to obtain a yellow pigment dispersion Y-1 with a solids concentration of 20% by weight and pigment/resin (weight ratio) = 60/40.

Production Example 4: Production of Blue Pigment Dispersion (B-1)

A blue pigment dispersion B-1 was obtained in the same manner as in the case of the red pigment dispersion R-1 except that organic pigment PB 15:6 (B-1, available from TOYO INK CO., LTD.) was used as a pigment.

[0129]

Production Example 5: Production of Yellow Pigment Dispersion (Y-1)

A yellow pigment dispersion Y-1 was obtained in the same manner as in the case of the red pigment dispersion R-1 except that organic pigment PY139 (Y-1, available from Clariant) was used as a pigment.

[0130]

Example 1

The carbon black dispersion CB-1 (267.9 g) and titanium black dispersion TB-1 (267.9 g) were mixed, and a solution obtained by dissolving a 40% by weight solution (122.1 g) of the acryl polymer (P-1) in propylene glycol monoethyl ether acetate, a 50% by weight solution (94.6 g) of dipentaerythritol hexaacrylate (DPHA manufactured by Nippon Kayaku Co., Ltd.) as a multi-functional monomer in propylene glycol monomethyl ether acetate, "ADEKA ARKLS" NCI-831 (11.8 g) available from ADEKA CORPORATION as a photopolymerization initiator, a silane coupling agent mixed solution (a-1) (37.5 g) as an adhesion promoter, and a 10% by weight solution (4.0 g) of propylene glycol monomethyl ether acetate which is a

silicone-base surfactant, in propylene glycol monomethyl ether acetate (194.0 g) were added thereto to obtain a black resin composition 1 with a total solids concentration of 25% by weight and pigment/resin (weight ratio) = 45/55.

[0131]

5 The black resin composition 1 was applied onto a soda glass substrate using a spinner 1H-DS manufactured by MIKASA CO., LTD. and prebaked at 100°C for 10 minutes to produce a coated film. Using a mask aligner PEM-6M manufactured by UNION OPTICAL CO., LTD., the coated film was exposed (200 mJ/cm²) through a photomask, developed using a 0.045% by weight aqueous KOH solution, and then
10 washed with pure water to obtain a patterning substrate. Further, the patterning substrate was cured at 230°C for 30 minutes. In this manner, a black matrix 1 with a thickness of 1.00 μm was prepared.

[0132]

Example 2

15 A black resin composition 2 was obtained in the same manner as in Example 1 except that the silane coupling agent mixed solution (a-2) was used instead of the silane coupling agent mixed solution (a-1).

[0133]

20 A black matrix 2 with a thickness of 1.00 μm was prepared in the same manner as in Example 1 using the black resin composition 2.

[0134]

Example 3

25 A black resin composition 3 was obtained in the same manner as in Example 1 except that the silane coupling agent mixed solution (a-3) was used instead of the silane coupling agent mixed solution (a-1).

[0135]

A black matrix 3 with a thickness of 1.00 μm was prepared in the same

manner as in Example 1 using the black resin composition 3.

[0136]

Example 4

A black resin composition 4 was obtained in the same manner as in Example
5 1 except that the amount of added silane coupling agent mixed solution (a-1) was 6.3 g, and the amount of added propylene glycol monomethyl ether acetate was 225.2 g.

[0137]

A black matrix 4 with a thickness of 1.00 μm was prepared in the same
manner as in Example 1 using the black resin composition 4.

10 [0138]

Example 5

A black resin composition 5 was obtained in the same manner as in Example
1 except that the amount of added silane coupling agent mixed solution (a-1) was
12.5 g, and the amount of added propylene glycol monomethyl ether acetate was
15 219.0 g.

[0139]

A black matrix 5 with a thickness of 1.00 μm was prepared in the same
manner as in Example 1 using the black resin composition 5.

[0140]

20 Example 6

A black resin composition 6 was obtained in the same manner as in Example
1 except that the amount of added silane coupling agent mixed solution (a-1) was
62.5 g, and the amount of added propylene glycol monomethyl ether acetate was
169.0 g.

25 [0141]

A black matrix 6 with a thickness of 1.00 μm was prepared using the black
resin composition 6 in the same manner as in Example 1.

[0142]

Example 7

A black resin composition 7 was obtained in the same manner as in Example 1 except that the amount of added silane coupling agent mixed solution (a-1) was 187.5 g, and the amount of added propylene glycol monomethyl ether acetate was 44.0 g.

[0143]

A black matrix 7 with a thickness of 1.00 μm was prepared using the black resin composition 7 in the same manner as in Example 1.

[0144]

Example 8

A black resin composition 8 was obtained in the same manner as in Example 1 except that 7.5 g of 3-methacryloxypropyltrimethoxysilane (a-8) was added in addition to silane coupling agent mixed solution (a-1), and the amount of added propylene glycol monomethyl ether acetate was 186.5 g.

[0145]

A black matrix 8 with a thickness of 1.00 μm was prepared using the black resin composition 8 in the same manner as in Example 1.

[0146]

Example 9

A black resin composition 9 was obtained in the same manner as in Example 8 except that the amount of added silane coupling agent mixed solution (a-1) was 12.5 g, and the amount of added propylene glycol monomethyl ether acetate was 211.5 g.

[0147]

A black matrix 9 with a thickness of 1.00 μm was prepared using the black resin composition 9 in the same manner as in Example 1.

[0148]

Example 10

A black resin composition 10 was obtained in the same manner as in Example 8 except that the amount of added silane coupling agent mixed solution (a-1) was 62.5 g, and the amount of added propylene glycol monomethyl ether acetate was 161.5 g.

[0149]

A black matrix 10 with a thickness of 1.00 μm was prepared using the black resin composition 10 in the same manner as in Example 1.

[0150]

Example 11

A black resin composition 11 was obtained in the same manner as in Example 8 except that the amount of added carbon black dispersion CB-1 was 0 g, and the amount of added titanium black dispersion TB-1 was 534.8 g.

[0151]

A black matrix 11 with a thickness of 1.00 μm was prepared using the black resin composition 11 in the same manner as in Example 1.

[0152]

Example 12

A black resin composition 12 was obtained in the same manner as in Example 8 except that the amount of added carbon black dispersion CB-1 was 134.0 g, and the amount of added titanium black dispersion TB-1 was 401.9 g.

[0153]

A black matrix 12 with a thickness of 1.00 μm was prepared using the black resin composition 12 in the same manner as in Example 1.

[0154]

Example 13

A black resin composition 13 was obtained in the same manner as in Example 8 except that the amount of added carbon black dispersion CB-1 was 401.9 g, and the amount of added titanium black dispersion TB-1 was 134.0 g.

[0155]

5 A black matrix 13 with a thickness of 1.00 μm was prepared using the black resin composition 13 in the same manner as in Example 1.

[0156]

Example 14

10 A black resin composition 14 was obtained in the same manner as in Example 8 except that the amount of added carbon black dispersion CB-1 was 534.8 g, and the amount of added titanium black dispersion TB-1 was 0 g.

[0157]

A black matrix 14 with a thickness of 1.00 μm was prepared using the black resin composition 14 in the same manner as in Example 1.

15 [0158]

Example 15

20 The red pigment dispersion R-1 (160.2 g), blue pigment dispersion B-1 (320.4 g) and yellow pigment dispersion Y-1 (320.4 g) were mixed, and a solution obtained by dissolving a 40% by weight solution (64.8 g) of the acryl polymer (P-1) in propylene glycol monoethyl ether acetate, a 50% by weight solution (38.7 g) of dipentaerythritol hexaacrylate (DPHA manufactured by Nippon Kayaku Co., Ltd.) as a multi-functional monomer in propylene glycol monomethyl ether acetate, "ADEKA ARKLS" NCI-831 (9.7 g) available from ADEKA CORPORATION as a photopolymerization initiator, silane coupling agent mixed solution (a-1) (30.0 g) as an adhesion promoter, 3-methacryloxypropyltrimethoxysilane (a-8) (7.5 g), a 10% by weight solution (4.0 g) of propylene glycol monomethyl ether acetate which is a silicone-base surfactant, in propylene glycol monomethyl ether acetate (44.3 g) were

25

added thereto to obtain a pseudo black resin composition 15 with a total solids concentration of 25% by weight and pigment/resin (weight ratio) = 40/60.

[0159]

A black matrix 15 with a thickness of 1.00 μm was prepared using the black resin composition 15 in the same manner as in Example 1.

[0160]

Comparative Example 1

A black resin composition 16 was obtained in the same manner as in Example 1 except that 7.5 g of 3-methacryloxypropyltrimethoxysilane (a-8) was added without adding the silane coupling agent mixed solution (a-1), and the amount of added propylene glycol monomethyl ether acetate was 224.0 g.

[0161]

A black matrix 16 with a thickness of 1.00 μm was prepared using the black resin composition 16 in the same manner as in Example 1.

[0162]

Comparative Example 2

A black resin composition 17 was obtained in the same manner as in Example 1 except that the silane coupling agent mixed solution (a-4) was used instead of the silane coupling agent mixed solution (a-1).

[0163]

A black matrix 17 with a thickness of 1.00 μm was prepared using the black resin composition 17 in the same manner as in Example 1.

[0164]

Comparative Example 3

A black resin composition 18 was obtained in the same manner as in Example 1 except that the silane coupling agent mixed solution (a-5) was used instead of the silane coupling agent mixed solution (a-1).

[0165]

A black matrix 18 with a thickness of 1.00 μm was prepared using the black resin composition 18 in the same manner as in Example 1.

[0166]

5 Comparative Example 4

A black resin composition 19 was obtained in the same manner as in Example 1 except that the silane coupling agent mixed solution (a-6) was used instead of the silane coupling agent mixed solution (a-1).

[0167]

10 A black matrix 19 with a thickness of 1.00 μm was prepared using the black resin composition 19 in the same manner as in Example 1.

[0168]

Comparative Example 5

15 A black resin composition 20 was obtained in the same manner as in Example 1 except that the silane coupling agent mixed solution (a-7) was used instead of the silane coupling agent mixed solution (a-1).

[0169]

A black matrix 20 with a thickness of 1.00 μm was prepared using the black resin composition 20 in the same manner as in Example 1.

20 [0170]

Comparative Example 6

A black resin composition 21 was obtained in the same manner as in Example 1 except that 7.5 g of 3-methacryloxypropyltrimethoxysilane (a-9) was added instead of the silane coupling agent mixed solution (a-1), and the amount of added propylene glycol monomethyl ether acetate was 224.0 g.

25

[0171]

A black matrix 21 with a thickness of 1.00 μm was prepared using the black

resin composition 21 in the same manner as in Example 1.

[0172]

Comparative Example 7

5 A black resin composition 22 was obtained in the same manner as in Example 1 except that 7.5 g of 3-aminopropyltriethoxysilane (a-10) was added instead of the silane coupling agent mixed solution (a-1), and the amount of added propylene glycol monomethyl ether acetate was 224.0 g.

[0173]

10 A black matrix 22 with a thickness of 1.00 μm was prepared using the black resin composition 22 in the same manner as in Example 1.

[0174]

Comparative Example 8

15 A black resin composition 23 was obtained in the same manner as in Example 1 except that 7.5 g of 3-ureidopropyltriethoxysilane (a-11) was added instead of the silane coupling agent mixed solution (a-1), and the amount of added propylene glycol monomethyl ether acetate was 224.0 g.

[0175]

A black matrix 23 with a thickness of 1.00 μm was prepared using the black resin composition 23 in the same manner as in Example 1.

20 [0176]

Comparative Example 9

25 A black resin composition 24 was obtained in the same manner as in Example 1 except that 7.5 g of 3-triethoxysilyl-N-(1,3-dimethyl-butylidene)propylamine (a-12) was added instead of the silane coupling agent mixed solution (a-1), and the amount of added propylene glycol monomethyl ether acetate was 224.0 g.

[0177]

A black matrix 24 with a thickness of 1.00 μm was prepared using the black

resin composition 24 in the same manner as in Example 1.

[0178]

The evaluation results are shown in Table 1. It can be seen that the black matrixes formed by using the resin compositions described in Examples have a high
5 adhesion and an excellent chemical resistance, and the black matrix is not peeled easily even after the moist heat treatment and the immersion in chemicals.

[0179]

Table 1		Black Resin Composition		Composition of Resin Composition										Evaluation Results of Resin Black Matrix													
				Pigment (A)		Alkali-Soluble Resin (B)		Silane Coupling Agent Mixed Solution (C1)				Silane Coupling Agent (C2)		Adhesion		Chemical Resistance		Resolution (μm)		Surface Resistance [Ω/□]		Reflected Light Chromaticity					
								Titanium Nitride / Carbon Black	Pseudo Black Pigment	Polymer	Polymer / Monomer	Weight Ratio (A)/(B)	Name											n [Formula (C1)]	Weight Ratio (C1)/((A)+(B))	Name	Weight Ratio (C2)/((A)+(B))
Example 1	BK-1	(TB-1)/(CB-1)=50/50		P-1		60/40	45/55	a-1	0	3/100	-	-	-	5	4	4	4	5	3.2	>10 ¹⁵	0.5	0.4					
Example 2	BK-2	(TB-1)/(CB-1)=50/50		P-1		60/40	45/55	a-2	0	3/100	-	-	-	5	4	4	3	5	3.2	>10 ¹⁵	0.5	0.4					
Example 3	BK-3	(TB-1)/(CB-1)=50/50		P-1		60/40	45/55	a-3	1	3/100	-	-	-	5	4	4	3	5	3.2	>10 ¹⁵	0.5	0.4					
Example 4	BK-4	(TB-1)/(CB-1)=50/50		P-1		60/40	45/55	a-1	0	0.5/100	-	-	-	5	3	4	3	5	3.2	>10 ¹⁵	0.5	0.4					
Example 5	BK-5	(TB-1)/(CB-1)=50/50		P-1		60/40	45/55	a-1	0	1/100	-	-	-	5	4	4	4	5	3.2	>10 ¹⁵	0.5	0.4					
Example 6	BK-6	(TB-1)/(CB-1)=50/50		P-1		60/40	45/55	a-1	0	5/100	-	-	-	5	4	5	5	8	3.2	>10 ¹⁵	0.5	0.4					
Example 7	BK-7	(TB-1)/(CB-1)=50/50		P-1		60/40	45/55	a-1	0	15/100	-	-	-	5	4	5	5	20	3.2	>10 ¹⁵	0.5	0.4					
Example 8	BK-8	(TB-1)/(CB-1)=50/50		P-1		60/40	45/55	a-1	0	3/100	a-8	3/100	5	5	5	5	5	5	3.2	>10 ¹⁵	0.5	0.4					
Example 9	BK-9	(TB-1)/(CB-1)=50/50		P-1		60/40	45/55	a-1	0	1/100	a-8	3/100	5	5	5	5	5	5	3.2	>10 ¹⁵	0.5	0.4					
Example 10	BK-10	(TB-1)/(CB-1)=50/50		P-1		60/40	45/55	a-1	0	5/100	a-8	3/100	5	5	5	5	5	8	3.2	>10 ¹⁵	0.5	0.4					
Example 11	BK-11	(TB-1)=100		P-1		60/40	45/55	a-1	0	3/100	a-8	3/100	5	5	5	5	5	5	3.6	>10 ¹⁵	2.1	1.8					
Example 12	BK-12	(TB-1)/(CB-1)=75/25		P-1		60/40	45/55	a-1	0	3/100	a-8	3/100	5	5	5	5	5	5	3.4	>10 ¹⁵	1.4	1.0					
Example 13	BK-13	(TB-1)/(CB-1)=25/75		P-1		60/40	45/55	a-1	0	3/100	a-8	3/100	5	5	4	4	4	8	3.0	2×10 ¹⁴	0.3	0.3					
Example 14	BK-14	(CB-1)=100		P-1		60/40	45/55	a-1	0	3/100	a-8	3/100	5	3	3	3	3	15	2.8	8×10 ¹²	0.1	0.2					
Example 15	BK-15	(R-1)/(B-1)/(Y-1)=20/40/40		P-1		60/40	40/60	a-1	0	3/100	a-8	3/100	5	4	4	4	4	15	1.5	>10 ¹⁵	0.0	-0.5					
Comparative Example 1	BK-16	(TB-1)/(CB-1)=50/50		P-1		60/40	45/55	-	-	-	a-8	3/100	5	2	3	2	5	3.2	>10 ¹⁵	0.5	0.4						
Comparative Example 2	BK-17	(TB-1)/(CB-1)=50/50		P-1		60/40	45/55	a-4	2	3/100	-	-	4	1	3	1	5	3.2	>10 ¹⁵	0.5	0.4						
Comparative Example 3	BK-18	(TB-1)/(CB-1)=50/50		P-1		60/40	45/55	a-5	2	3/100	-	-	4	1	3	1	5	3.2	>10 ¹⁵	0.5	0.4						
Comparative Example 4	BK-19	(TB-1)/(CB-1)=50/50		P-1		60/40	45/55	a-6	-	3/100	-	-	4	1	3	1	5	3.2	>10 ¹⁵	0.5	0.4						
Comparative Example 5	BK-20	(TB-1)/(CB-1)=50/50		P-1		60/40	45/55	a-7	-	3/100	-	-	4	2	3	2	5	3.2	>10 ¹⁵	0.5	0.4						
Comparative Example 6	BK-21	(TB-1)/(CB-1)=50/50		P-1		60/40	45/55	-	-	-	a-9	3/100	4	2	3	1	5	3.2	>10 ¹⁵	0.5	0.4						
Comparative Example 7	BK-22	(TB-1)/(CB-1)=50/50		P-1		60/40	45/55	-	-	-	a-10	3/100	3	0	1	0	10	2.9	>10 ¹⁵	0.5	0.4						
Comparative Example 8	BK-23	(TB-1)/(CB-1)=50/50		P-1		60/40	45/55	-	-	-	a-11	3/100	4	2	3	1	5	3.2	>10 ¹⁵	0.5	0.4						
Comparative Example 9	BK-24	(TB-1)/(CB-1)=50/50		P-1		60/40	45/55	-	-	-	a-12	3/100	4	0	3	0	5	3.2	>10 ¹⁵	0.5	0.4						

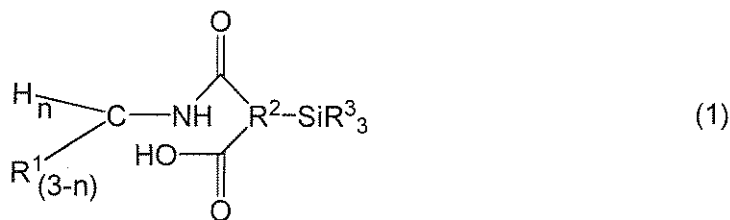
INDUSTRIAL APPLICABILITY

[0180]

The colored resin composition of the present invention may be utilized for a black matrix of a color filter substrate for liquid crystal displays.

CLAIMS

1. A colored resin composition comprising at least (A) a color pigment; (B) an alkali-soluble resin, (C) an adhesion promoter and (D) an organic solvent, said composition comprising as said (C) adhesion promoter at least a silane coupling agent represented by the Formula (1) below:



(wherein R^1 may be the same or different from each other and represents a C_1 - C_6 alkyl group which optionally has a substituent(s); n represents 0 or 1; R^2 represents a C_3 - C_{30} trivalent organic group; R^3 may be the same or different from each other and represents a C_1 - C_6 alkyl group, a C_1 - C_6 alkoxy group, a phenyl group, a hydroxyl group or a phenoxy group wherein each of the groups other than the hydroxyl group optionally has a substituent(s)).

2. The colored resin composition according to claim 1, wherein said (C) adhesion promoter is a silane coupling agent represented by said Formula (1) wherein $n = 0$.

3. The colored resin composition according to claim 1 or 2, which comprises at least two silane coupling agents as said (C) adhesion promoter.

4. The colored resin composition according to any one of claims 1 to 3, wherein said (A) color pigment is a black light-shielding material.

5. The colored resin composition according to claim 4, which comprises at least titanium nitride compound particles and/or carbon black as said black light-shielding material.

6. The colored resin composition according to claim 5, wherein the weight ratio of said titanium nitride compound particles to the total weight of said black light-

shielding material is 20 to 80% by weight.

7. A resin black matrix substrate obtained by applying said black resin composition according to any one of claims 4 to 6 onto a transparent substrate and forming a pattern.