

Description

Title of the invention: COLORING MATERIAL DISPERSION LIQUID AND PHOTSENSITIVE COLORING RESIN COMPOSITION

Technical field

[0001] The invention relates to a coloring material dispersion liquid, and a photosensitive coloring resin composition that uses the coloring material dispersion liquid.

Background art

[0002] In recent years, color liquid crystal display apparatuses (LCDs) have been rapidly spreading as flat displays of personal computers, cellular phones, etc. For example, color filters for LCDs are usually produced by a method in which different color phases, that is, red, green and blue, are sequentially formed in color patterns in a stripe manner, a mosaic manner, etc., on a surface of a transparent substrate made of a glass sheet, a plastic sheet, etc., provided with a black matrix. In both the colored layer and the black matrix, a coloring material dispersion technique plays an important role.

[0003] Furthermore, due to rise of various types of display apparatuses, such as organic EL displays, and diversification of information displayed, demands regarding the color characteristics of the aforementioned color filters for LCDs are escalating. In particular, demands for broader ranges of color reproducibility are strengthening. Therefore, as for the coloring materials for color filters, the technology for stably dispersing coloring materials at high concentrations is becoming important. Generally, a coloring material dispersion liquid is made up of a coloring material, a solvent, a dispersing agent and a binder resin. Adding a large amount of the dispersing agent into the composition makes it possible to stably disperse the coloring material. However, in a heating process for producing a color filter, there have occurred problems, such as a problem that the dispersing agent yellows, resulting in reduction in brightness, a problem that the concentration of an alkali-soluble photo-curing resin is diluted, giving rise to problems of reduced sensitivity, poor curing, reduced coating film strength, poor

development property, etc. In particular, the poor development property causes serious problems in production. Therefore, as for the coloring material dispersion liquid, securing stability of a pigment dispersion liquid by providing a binder resin itself with a high level of dispersion stability while using a minimum amount of a dispersing agent has been an issue. Moreover, since the demands for the color characteristics have diversified in recent year, development of coloring materials that use dyes or inorganic pigments as well as conventional organic pigments has proceeded. In the present situation, the conventional art finds it difficult to disperse and stabilize such diversified coloring materials at high concentrations.

[0004] Furthermore, in the field of touch panel displays with remarkable technological innovations, a black matrix is formed as a light blocking film, as is the case with the color filter, and it is a general practice to form the black matrix on a cover glass or a cover film that faces a sensor substrate by using a print ink. On another hand, the demand for weight reduction of touch panels is escalating, and development of technologies for forming a light blocking film and a touch sensor simultaneously on a cover glass is proceeding. In such a case, since there is a need to form electrodes and the like after forming the black matrix on the cover glass, a high heat resistance for withstanding a process of forming electrodes in a high-temperature vacuum is demanded.

[0005] As pigments used in the black matrix, carbon black, titanium blacks, such as lower-order titanium oxide and titanium oxynitride, metal oxides such as iron oxide, and organic pigment mixed-colors, are used; however, carbon black and titanium oxynitride have become mainstream pigments. In order to obtain a black matrix having high insulating property, a carbon black subjected to surface treatment with titanium black, a resin, etc., as a light blocking material, or a mixture of organic pigments is used (refer to, e.g., the Patent document 1). However, in order to obtain high light blocking property, there is a need to stably disperse various pigments at high pigment concentrations, which, according to the conventional art, is insufficiently met from the viewpoint of long-term preservation stability.

[0006] As a technology for stabilizing the dispersion by using a small amount of a

dispersion agent, a technology that employs a high-molecular dispersing agent having both an acid value and an amine value and a copolymer having an imide group and a photo-curing functional group has been disclosed (refer to, e.g., the Patent document 2). However, the technology is insufficient to disperse and stabilize a coloring material that is difficult to disperse, such as a titanium black and a carbon black. Besides, as a technology for stably dispersing a pigment even at a high pigment concentration, there can be cited a technology that use an acid-number dispersing agent having an acid value and an amine-number dispersing agent having an amine value in combination (refer to, e.g., the Patent document 3) and a technology that employs a resin-type dispersing agent that has a block structure having both a basic block and an acidic block (refer to, e.g., the Patent document 4). These technologies are useful for coloring liquids for inkjet coating, but it is difficult to apply the technologies to coloring liquids for photolithography which require photosensitivity and development property.

[0007] On another hand, as an acrylic resin for dispersing a pigment, there can be cited an acryl copolymer having in a side chain thereof a carboxyl group and an acryloyl group or a methacrylo group (refer to, e.g., the Patent document 5), and an acrylic resin having an acid value or an amine value at a specific molecular weight or hydroxyl group value (refer to, e.g., the Patent document 6). However, either one of them is insufficient from the viewpoint of achieving good levels in all of dispersion stability, photosensitivity and development property.

Prior-art documents

Patent documents

[0008] Patent document 1: Japanese Unexamined Patent Publication (Kokai) No. 2010-95716

Patent document 2: Japanese Patent No. 4195323

Patent document 3: Japanese Patent No. 4544292

Patent document 4: Japanese Unexamined Patent Publication (Kokai) No. 2009-167303

Patent document 5: Japanese Patent No. 3120476

Patent document 6: Japanese Unexamined Patent Publication (Kokai) No.

2003-171605

Summary of the invention

Problems to be solved by the invention

[0009] The invention was conceived in view of shortcomings of the conventional art mentioned above, and an object thereof is to provide a coloring material dispersion liquid that is excellent in dispersion stability and alkaline development solubility even in a composition that contains a coloring material at a high concentration. Furthermore, the invention also provides a photosensitive coloring resin composition excellent in preservation stability and plate-making characteristic by employing the coloring material dispersion liquid.

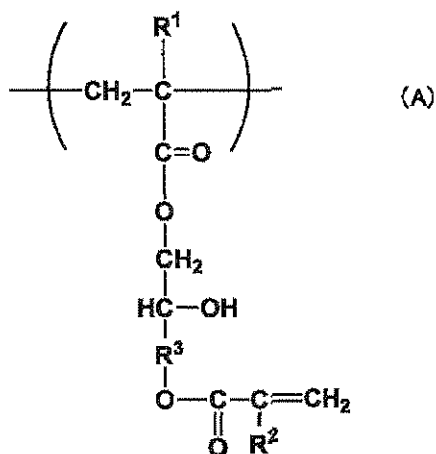
Means of solving the problems

[0010] As a result of intensive studies performed for the purpose of solving the problems of the conventional art, the inventors have found that the problems of the invention can be solved by employing an acryl copolymer that has a specific structure as mentioned below when a coloring material is to be dispersed.

[0011] That is, the objects of the invention are achieved by the following constructions.

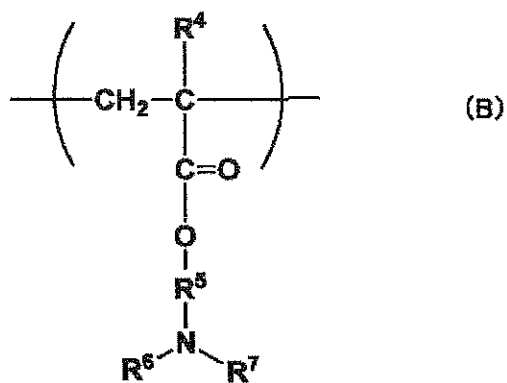
(1) A coloring material dispersion liquid containing at least a coloring material, an acryl copolymer and an organic solvent, the coloring material dispersion liquid being characterized in that the acryl copolymer has at least a structure represented by a formula (A) below which has in a side chain an ethylenic unsaturated group, a structure represented by a formula (B) below which has in a side chain a tertiary amino group and/or a structure represented by a formula (C) below which has in a side chain a quaternary ammonium salt, a structure (D) having in a side chain a carboxyl group, and a structure (E) having an aromatic ring, and that, as for the acryl copolymer, a base value is 5 to 70 mmol/100 g, an acid value is 50 to 120 mgKOH/g, and a weight-average molecular weight in terms of polystyrene by gel permeation chromatography is 5,000 to 30,000.

[Chem. 1]



(In the formula, R^1 and R^2 , independently of each other, represent a hydrogen atom or a methyl group, and R^3 represents a species selected from alkylene groups whose carbon number is 1 to 4, divalent alicyclic hydrocarbon groups whose carbon number is 3 to 6 and divalent aromatic hydrocarbon groups whose carbon number is 6 to 10.)

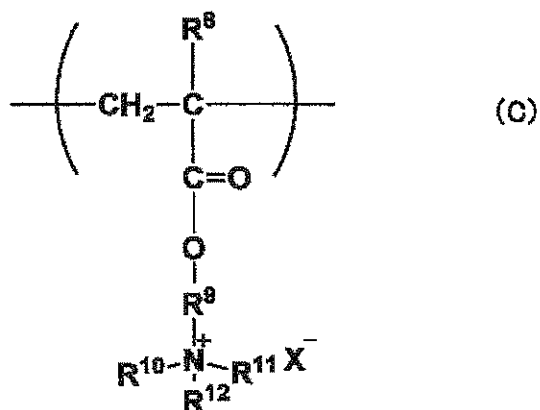
[Chem. 2]



(In the formula, R^4 represents a hydrogen atom or a methyl group, R^5 represents a species selected from alkylene groups whose carbon number is 1 to 4, divalent alkoxy groups whose carbon number is 1 to 4, divalent alicyclic hydrocarbon groups whose carbon number is 3 to 6 and divalent aromatic hydrocarbon groups whose carbon number is 6 to 10, and R^6 and R^7 , independently of each other, represent a species selected from alkyl groups whose carbon number is 1 to 4, alkoxy groups whose carbon number is 1 to 4, alicyclic hydrocarbon groups whose carbon number is 3 to 6 and aromatic hydrocarbon

groups whose carbon number is 6 to 10.)

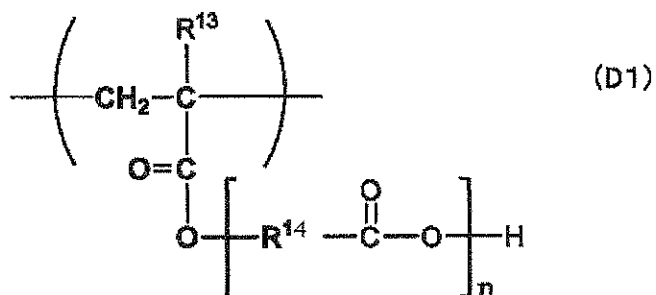
[Chem. 3]



(In the formula, R^8 represents a hydrogen atom or a methyl group, R^9 represents a species selected from alkylene groups whose carbon number is 1 to 4, divalent alkoxy groups whose carbon number is 1 to 4, divalent alicyclic hydrocarbon groups whose carbon number is 3 to 6 and divalent aromatic hydrocarbon groups whose carbon number is 6 to 10, R^{10} , R^{11} and R^{12} , independently of each other, represent a species selected from alkyl groups whose carbon number is 1 to 4, alkoxy groups whose carbon number is 1 to 4, alicyclic hydrocarbon groups whose carbon number is 3 to 6 and aromatic hydrocarbon groups whose carbon number is 6 to 10, and X represents any one of bromine, chlorine, iodine, hydrogen sulfate and hydroxide.)

[0012] (2) The coloring material dispersion liquid according to (1), wherein the structure (D) having the carboxyl group is represented by a formula (D1) below.

[Chem. 4]

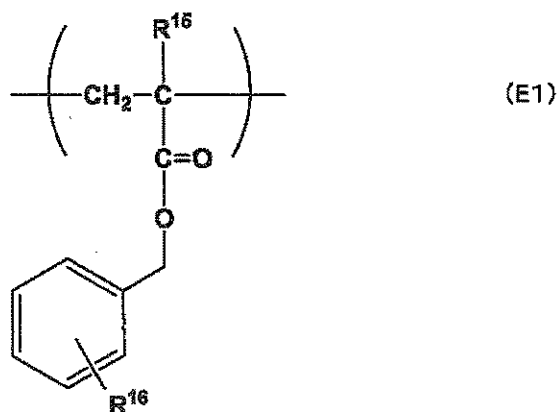


(In the formula, R^{13} represents a hydrogen atom or a methyl group, R^{14} represents a

species selected from alkylene groups whose carbon number is 1 to 4, divalent alicyclic hydrocarbon chains whose carbon number is 3 to 6 and divalent aromatic hydrocarbon chains whose carbon number is 6 to 10, and n represents an integer of 0 to 6, and n may be a single n or a mixture of a plurality of n's.)

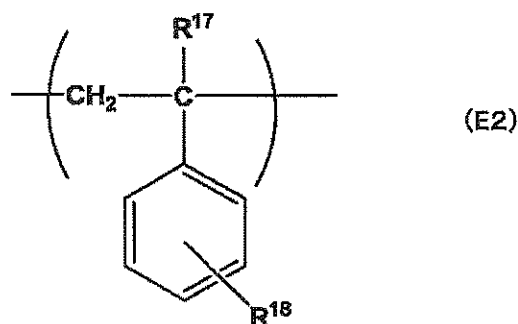
[0013] (3) The coloring material dispersion liquid according to (1) or (2), wherein the structure (E) having the aromatic ring is represented by a formula (E1) or (E2) below.

[Chem. 5]



(In the formula, R^{15} represents a hydrogen atom or a methyl group, and R^{16} represents a species selected from hydrogen, alkyl groups whose carbon number is 1 to 4, alkoxy groups whose carbon number is 1 to 4, alicyclic hydrocarbon groups whose carbon number is 3 to 6, aromatic hydrocarbon groups whose carbon number is 6 to 10, halogen atoms, ester groups, acyl groups and a nitro group.)

[Chem. 6]

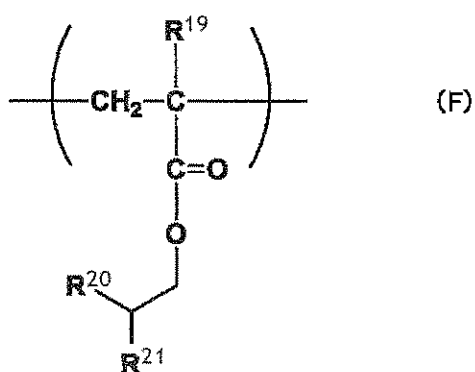


(In the formula, R^{17} represents a hydrogen atom or a methyl group, and R^{18} represents a species selected from hydrogen, alkyl groups whose carbon number is 1 to 4, alkoxy

groups whose carbon number is 1 to 4, alicyclic hydrocarbon groups whose carbon number is 3 to 6, aromatic hydrocarbon groups whose carbon number is 6 to 10, halogen atoms, ester groups, acyl groups and a nitro group.)

[0014] (4) The coloring material dispersion liquid according to (1), (2) or (3), wherein the acryl copolymer further has a structure represented by a formula (F) below which has in the side chain a carboxylic acid ester.

[Chem. 7]



(In the formula, R^{19} represents a hydrogen atom or a methyl group, R^{20} represents a hydrogen atom or an alkyl group whose carbon atom number 1 to 20, and R^{21} represents an alkyl group whose carbon atom number 2 to 40.)

[0015] (5) The coloring material dispersion liquid according to (4), wherein a total carbon number of the R^{20} and the R^{21} is greater than or equal to 4.

[0016] (6) The coloring material dispersion liquid according to any one of (3) to (5), having a structure represented by a formula (E2).

[0017] (7) The coloring material dispersion liquid according to any one of (1) to (6), containing, in addition to the acryl copolymer, a high-molecular dispersing agent that has at least a tertiary amino group.

[0018] (8) A photosensitive coloring resin composition containing at least the coloring material dispersion liquid according to any one of (1) to (7), a multifunctional acryl monomer and a photo-radical polymerization initiating agent.

Effect of the invention

[0019] The coloring material dispersion liquid of the invention attains characteristics

excellent in dispersion stability and alkaline development solubility even if a coloring material is contained at high concentration. By employing this coloring material dispersion liquid, a photosensitive coloring resin composition excellent in preservation stability and plate-making characteristic can be attained.

Description of embodiments

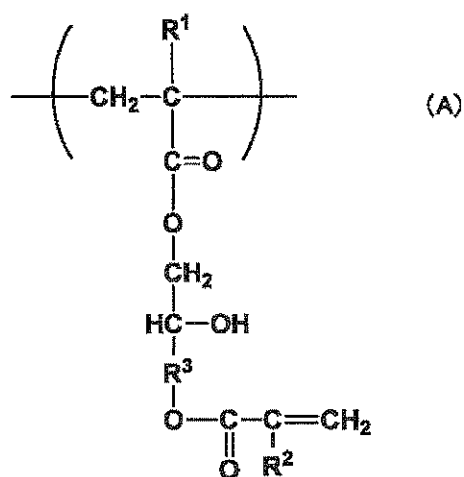
[0020] Hereinafter, the invention will further described in detail.

[0021] The coloring material dispersion liquid of the invention is characterized by being made up of at least a coloring material, an acryl copolymer having a specific structure, and an organic solvent.

[0022] The acryl copolymer used in the invention is characterized by having in a side chain a tertiary amino group and/or a quaternary ammonium salt, a carboxyl group and an aromatic ring, and further containing an ethylenic unsaturated bond in the acryl copolymer side chain.

[0023] The acryl copolymer used in the invention shall have a photosensitivity, that is, invariably has an acryl unit or a methacryl unit represented by a formula (A) below which has in a side chain thereof an ethylenic unsaturated group in order to manifest a function in which the acryl copolymer itself is taken into a crosslinking reaction, in the case where an initiating agent that produces a radical, an anion or a cation by an activation energy ray such as an ultraviolet ray (UV) is used together.

[Chem. 8]



(In the formula, R^1 and R^2 , independently of each other, represent a hydrogen atom or a methyl group, and R^3 represents a species selected from alkylene groups whose carbon number is 1 to 4, divalent alicyclic hydrocarbon groups whose carbon number is 3 to 6 and divalent aromatic hydrocarbon groups whose carbon number is 6 to 10.)

[0024] In the formula (A), R^1 and R^2 represent, independently of each other, a hydrogen atom or a methyl group, and when R^1 is hydrogen, an acryl unit is formed, and when R^1 is a methyl group, a methacryl unit is formed. R^3 is selected from alkylene groups whose carbon number is 1 to 4, divalent alicyclic hydrocarbon groups whose carbon number is 3 to 6 and divalent aromatic hydrocarbon groups whose carbon number is 6 to 10, and is preferred to be an alkylene group whose carbon number is 1 to 3, a divalent alicyclic hydrocarbon group whose carbon number is 5 to 6 or a divalent aromatic hydrocarbon group whose carbon number is 6 to 8.

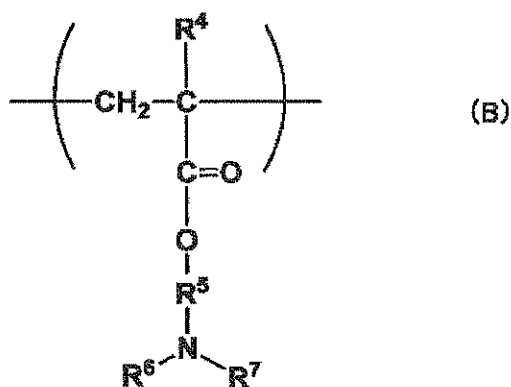
[0025] An introduction method for the (meth)acryl unit represented by the aforementioned formula (A) is not particularly limited, and the (meth)acryl unit can be introduced by an ordinary method. For example, a method in which a (meth)acryl copolymer obtained by copolymerizing a carboxyl group-containing unsaturated monomer is subjected to the addition reaction with a glycidyl group-containing polymerizable unsaturated monomer, or the like, can be cited. In this case, as the carboxyl group-containing unsaturated monomer to be copolymerized, acrylic acids, methacrylic acids, etc. can be cited as examples. As the glycidyl-containing unsaturated monomer, glycidyl acrylate, glycidyl methacrylate, etc. can be cited as examples. In the invention, these acryl monomers can be used singly or in a mixture of two or more species.

[0026] As for the acryl copolymer used in the invention, as a high level of dispersion stability is to be manifested, it is essential to contain a (meth)acryl unit represented by the formula (B) below which has in a side chain thereof a tertiary amino group and/or a (meth)acryl unit represented by the formula (C) below which has in a side chain thereof a quaternary ammonium salt.

[0027] Since the (meth)acryl unit represented by the formula (B) which has a tertiary

amino group and the (meth)acryl unit represented by the formula (C) which has in its side chain a quaternary ammonium salt both increase the affinity to the coloring material and improve the dispersion stability, it is permissible to introduce either one or both of them. In the case of application where development property is needed as in the invention, it is preferred to introduce the (meth)acryl unit of the formula (B) which has a tertiary amino group, from the viewpoint of ease of attaining a balance between development property and dispersion stability.

[Chem. 9]



(In the formula, R^4 represents a hydrogen atom or a methyl group, R^5 represents a species selected from alkylene groups whose carbon number is 1 to 4, divalent alkoxy groups whose carbon number is 1 to 4, divalent alicyclic hydrocarbon groups whose carbon number is 3 to 6 and divalent aromatic hydrocarbon groups whose carbon number is 6 to 10, and R^6 and R^7 , independently of each other, represent a species selected from alkyl groups whose carbon number is 1 to 4, alkoxy groups whose carbon number is 1 to 4, alicyclic hydrocarbon groups whose carbon number is 3 to 6 and aromatic hydrocarbon groups whose carbon number is 6 to 10.)

[0028] In the aforementioned formula (B), R^4 is a hydrogen atom or a methyl group, and when R^4 is hydrogen, an acryl unit is formed, and when R^4 is a methyl group, a methacryl unit is formed. R^5 is selected from alkylene groups whose carbon number is 1 to 4, divalent alkoxy groups whose carbon number is 1 to 4, divalent alicyclic hydrocarbon groups whose carbon number is 3 to 6 and divalent aromatic hydrocarbon

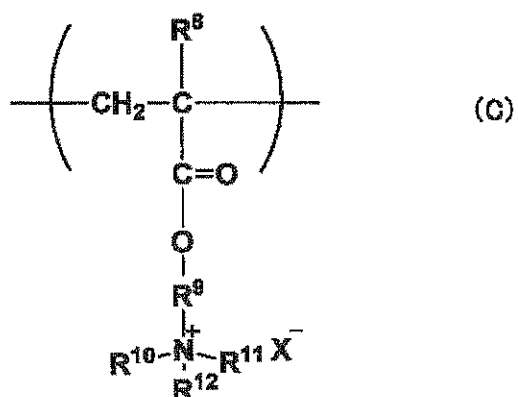
groups whose carbon number is 6 to 10, and is preferred to be an alkylene group whose carbon number is 1 to 3, a divalent alicyclic hydrocarbon group whose carbon number is 5 to 6 or a divalent aromatic hydrocarbon group whose carbon number is 6 to 8.

[0029] R^6 and R^7 are independent of each other, and may be the same or different, and are each selected from alkyl groups whose carbon number is 1 to 4, alkoxy groups whose carbon number is 1 to 4, alicyclic hydrocarbon groups whose carbon number is 3 to 6 and aromatic hydrocarbon groups whose carbon number is 6 to 10, and are each preferred to be an alkylene group whose carbon number is 1 to 3, an alkoxy group whose carbon number is 1 to 3, a divalent alicyclic hydrocarbon group whose carbon number is 5 to 6 or a divalent aromatic hydrocarbon group whose carbon number is 6 to 8.

[0030] As an unsaturated monomer that constitutes the (meth)acryl unit having a tertiary amino group which is represented by the formula (B), there can be cited, as examples, acrylic acid-2-dimethylaminoethyl, acrylic acid-2-diethylaminoethyl, acrylic acid-2-dipropylaminoethyl, acrylic acid-2-diphenylaminoethyl, acrylic acid-2-dibenzylaminoethyl, methacrylic acid-2-dimethylaminoethyl, methacrylic acid-2-diethylaminoethyl, methacrylic acid-2-dipropylaminoethyl, methacrylic acid-2-diphenylaminoethyl, methacrylic acid-2-benzylaminoethyl, etc. However, the unsaturated monomer is not particularly limited. These (meth)acryl monomers may be used singly or may also be used in a mixture of two or more species.

[0031] The (meth)acryl unit having a tertiary amino group which is represented by the formula (B) can be introduced by copolymerizing an unsaturated monomer that contains an amino group.

[0032] [Chem. 10]



(In the formula, R^8 represents a hydrogen atom or a methyl group, R^9 represents a species selected from alkylene groups whose carbon number is 1 to 4, divalent alkoxy groups whose carbon number is 1 to 4, divalent alicyclic hydrocarbon groups whose carbon number is 3 to 6 and divalent aromatic hydrocarbon groups whose carbon number is 6 to 10, R^{10} , R^{11} and R^{12} , independently of each other, represent a species selected from alkyl groups whose carbon number is 1 to 4, alkoxy groups whose carbon number is 1 to 4, alicyclic hydrocarbon groups whose carbon number is 3 to 6 and aromatic hydrocarbon groups whose carbon number is 6 to 10, and X represents any one of bromine, chlorine, iodine, hydrogen sulfate and hydroxide.)

[0033] In the aforementioned formula (C), R^8 is a hydrogen atom or a methyl group, and when R^8 is hydrogen, an acryl unit is formed, and when R^8 is a methyl group, a methacryl unit is formed. R^9 is selected from alkylene groups whose carbon number is 1 to 4, divalent alkoxy groups whose carbon number is 1 to 4, divalent alicyclic hydrocarbon groups whose carbon number is 3 to 6 and divalent aromatic hydrocarbon groups whose carbon number is 6 to 10, and is preferred to be an alkylene group whose carbon number is 1 to 3, a divalent alicyclic hydrocarbon group whose carbon number is 5 to 6 or a divalent aromatic hydrocarbon group whose carbon number is 6 to 8.

[0034] R^{10} , R^{11} and R^{12} are independent of each other, and may be the same or different, and are each selected from alkyl groups whose carbon number is 1 to 4, alkoxy groups whose carbon number is 1 to 4, alicyclic hydrocarbon groups whose carbon

number is 3 to 6 and aromatic hydrocarbon group whose carbon number is 6 to 10, and are each preferred to be an alkylene group whose carbon number is 1 to 3, an alkoxy group whose carbon number is 1 to 3, a divalent alicyclic hydrocarbon group whose carbon number is 5 to 6 or a divalent aromatic hydrocarbon group whose carbon number is 6 to 8.

[0035] X is selected from bromine, chlorine, iodine, hydrogen sulfate and hydroxide, and is preferred to be bromine or chlorine.

[0036] As an unsaturated monomer that constitutes the (meth)acryl unit having a quaternary ammonium salt which is represented by the formula (C), there are cited, as examples, acrylic acid-dimethylaminoethyl methyl chloride salts, acrylic acid dimethylaminoethyl benzyl chloride salts, methacrylic acid-dimethylaminoethyl methyl chloride salts, methacrylic acid dimethylaminoethyl benzyl chloride salts, etc., but the unsaturated monomer that constitutes the (meth)acryl unit is not particularly limited. These (meth)acryl monomers may be used singly or may also be used in a mixture of two or more species.

[0037] The (meth)acryl unit having a quaternary ammonium salt which is represented by the formula (C) can be introduced by copolymerizing an unsaturated monomer that contains a quaternary ammonium salt.

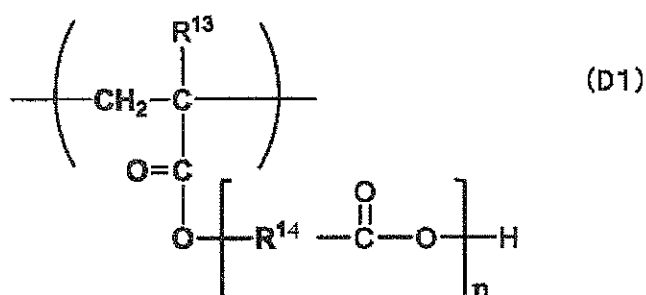
[0038] From the view point of industrial use, a tertiary amine, such as methacrylic acid-2-dimethylaminoethyl, is preferred. In the invention, the acryl monomer represented by the formula (B) and/or (C) may be used singly or may also be used in a mixture of two or more species.

[0039] As for the acryl copolymer used in the invention, as alkaline development property is to be given, it is essential to have in its side chain an acidic group such as a carboxyl group, a sulfonic acid group or a phosphoric acid group. In the invention, the acryl copolymer invariably has a structure (D) that has in a molecular side chain a carboxyl group.

[0040] The structure (D) having a carboxyl group as mentioned above can be introduced by copolymerizing a carboxyl group-containing unsaturated monomer. As

the carboxyl group-containing unsaturated monomer, there can be cited, as examples, acrylic acid, methacrylic acid, itaconic acid, maleic acid, maleic anhydride, phthalic acid, phthalic anhydride, crotonic acid, etc. As the structure (D) having a carboxyl group, a carboxy group-containing unsaturated monomer represented by the formula (D1) below is preferred from the viewpoint of stability and control of reaction, taking into consideration that the (meth)acryl unit having in its molecular side chain an ethylenic unsaturated group which is represented by the formula (A) described above is introduced.

[Chem. 11]



(In the formula, R^{13} represents a hydrogen atom or a methyl group, R^{14} represents a species selected from alkylene groups whose carbon number is 1 to 4, divalent alicyclic hydrocarbon chains whose carbon number is 3 to 6 and divalent aromatic hydrocarbon chains whose carbon number is 6 to 10, and n represents an integer of 0 to 6, and n may be a single n or a mixture of a plurality of n 's.)

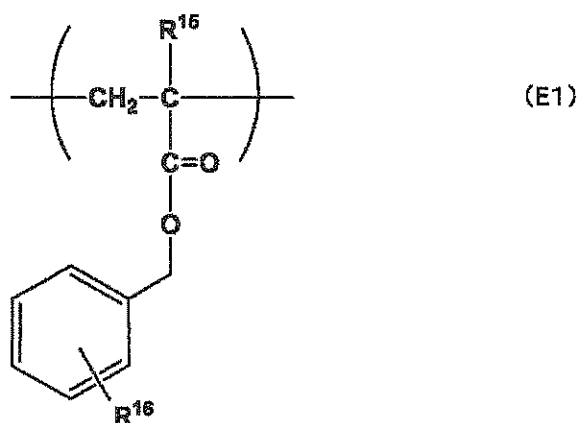
[0041] In the aforementioned formula (D1), R^{13} is a hydrogen atom or a methyl group, and when R^{13} is hydrogen, an acryl unit is formed, and when R^{13} is a methyl group, a methacryl unit acid is formed. R^{14} is selected from alkylene groups whose carbon number is 1 to 4, divalent alicyclic hydrocarbon groups whose carbon number is 3 to 6 and divalent aromatic hydrocarbon groups whose carbon number is 6 to 10, and is preferred to be an alkylene group whose carbon number is 1 to 3, a divalent alicyclic hydrocarbon group whose carbon number is 5 to 6 or a divalent aromatic hydrocarbon group whose carbon number is 6 to 8. n is an integer of 0 to 6, and is preferred to be 0. n may be an integer, or a plurality of integers of 0 to 6.

[0042] As an unsaturated monomer (D1) containing a carboxyl group which is represented by the aforementioned structure, there can be cited, as examples, acrylic acid,

methacrylic acid, 2-carboxy ethyl acrylate oligomers, 2-carboxy ethyl methacrylate oligomers, etc. These (meth)acryl monomers may be used singly or may also be used in a mixture of two or more species.

[0043] The acryl copolymer of the invention invariably has a structure (E) that has in a side chain an aromatic ring, as a high level of heat resistance is to be manifested. The structure (E) having in its side chain an aromatic ring can be introduced by copolymerizing an unsaturated monomer that has an aromatic ring. As the structure (E), benzyl groups and derivatives of benzyl groups as in the formula (E1) below or phenyl groups and derivatives of phenyl groups as in the formula (E2) are particularly suitable, and attain effects of high level of heat resistance improvement.

[Chem. 12]



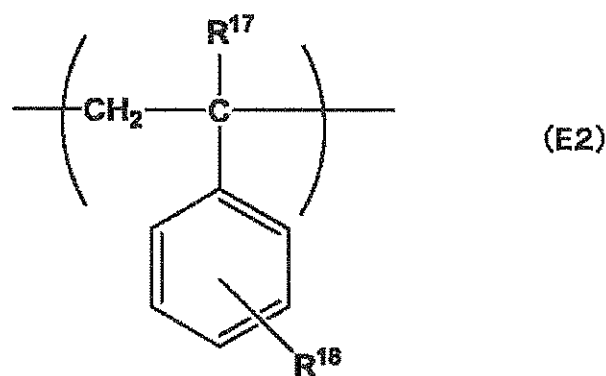
(In the formula, R^{15} represents a hydrogen atom or a methyl group, and R^{16} represents a species selected from hydrogen, alkyl groups whose carbon number is 1 to 4, alkoxy groups whose carbon number is 1 to 4, alicyclic hydrocarbon groups whose carbon number is 3 to 6, aromatic hydrocarbon groups whose carbon number is 6 to 10, halogen atoms, ester groups, acyl groups and a nitro group.)

[0044] In the aforementioned formula (E1), R^{15} is a hydrogen atom or a methyl group, and when R^{15} is hydrogen, an acryl unit is formed, and when R^{15} is a methyl group, a methacryl unit is formed. R^{16} is selected from hydrogen, alkyl groups whose carbon number is 1 to 4, alkoxy groups whose carbon number is 1 to 4, alicyclic hydrocarbon groups whose carbon number is 3 to 6, aromatic hydrocarbon groups whose carbon number is 6 to 10, halogen atoms, ester groups, acyl groups and a nitro group, and is

preferably hydrogen, an alkyl group whose carbon number is 1 to 3, an alkoxy group whose carbon number is 1 to 3, an alicyclic hydrocarbon group whose carbon number is 5 to 6 or an aromatic hydrocarbon group whose carbon number is 6 to 8.

[0045] As the (meth)acryl monomer containing an aromatic ring which is represented by the aforementioned formula (E1), for example, benzyl acrylate, benzyl methacrylate, etc., are cited as example; however, the (meth)acryl monomer containing an aromatic ring is not limited to these. In the invention, these (meth)acryl monomers may be used singly or may also be used in a mixture of two or more species.

[0046] [Chem. 13]



(In the formula, R^{17} represents a hydrogen atom or a methyl group, and in the formula, R^{18} represents a species selected from hydrogen, alkyl groups whose carbon number is 1 to 4, alkoxy groups whose carbon number is 1 to 4, alicyclic hydrocarbon groups whose carbon number is 3 to 6, aromatic hydrocarbon groups whose carbon number is 6 to 10, halogen atoms, ester groups, acyl groups and a nitro group.)

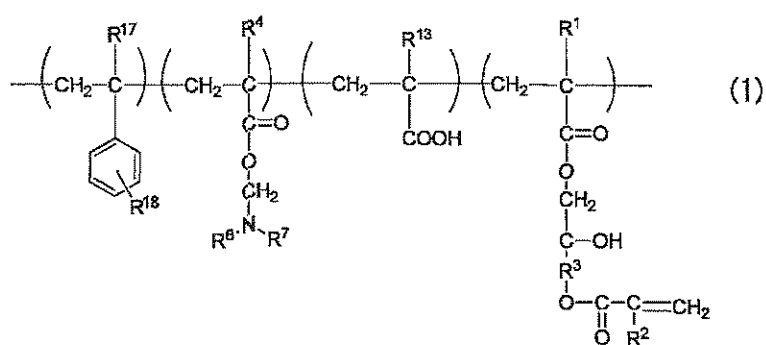
[0047] In the aforementioned formula (E2), R^{17} is a hydrogen atom or a methyl group, and when R^{17} is hydrogen, an acryl unit is formed, and when R^{17} is a methyl group, a methacryl unit is formed. R^{18} is a species selected from hydrogen, alkyl groups whose carbon number is 1 to 4, alkoxy groups whose carbon number is 1 to 4, alicyclic hydrocarbon groups whose carbon number is 3 to 6, aromatic hydrocarbon groups whose carbon number is 6 to 10, halogen atoms, ester groups, acyl groups and a nitro group, and is preferably hydrogen, an alkyl group whose carbon number is 1 to 3, an alkoxy group whose carbon number is 1 to 3, an alicyclic hydrocarbon group whose carbon number is 5

to 6 or an aromatic hydrocarbon group whose carbon number is 6 to 8.

[0048] As an unsaturated monomer containing an aromatic ring which is represented by the aforementioned formula (E2), for example, styrene, α -methylstyrene, 4-vinyltoluene and its structural isomer, 4-methoxystyrene and its structural isomers, 4-butoxystyrene and its structural isomers, 4-tert-butoxystyrene and its structural isomers, 4-vinylbiphenyl, 2-vinylnaphthalene and its structural isomers, 9-vinylanthracene, 9-vinylcarbazole, etc. can be cited. However, the unsaturated monomer containing an aromatic ring is not limited to these. In the invention, these acryl monomers may be used singly or may also be used in a mixture of two or more species.

[0049] The acryl copolymer is characterized by being made up of a structural unit that contains in its side chain a polymerizable unsaturated bond, a tertiary amino group and/or a quaternary ammonium salt, a carboxyl group and an aromatic ring. In particular, the acryl copolymer is preferred to contain a (meth)acryl unit that contains in its side chain a tertiary amino group. As a particularly preferable acryl copolymer, an acryl copolymer containing a structural unit represented by the formula (1) below is cited as an example. The acryl copolymer may contain another main chain constitutional unit according to needs.

[Chem. 14]

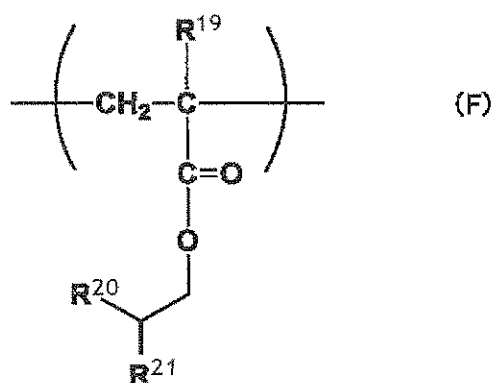


(In the formula, R^1 , R^2 , R^4 , R^{13} and R^{17} , independently of each other, represent a hydrogen atom or a methyl group, R^3 represents a species selected from alkylene groups whose carbon number is 1 to 4, divalent alicyclic hydrocarbon groups whose carbon number is 3 to 6 and divalent aromatic hydrocarbon group whose carbon number is 6 to 10, R^6 and R^7 , independently of each other, represent a species selected from alkyl groups

whose carbon number is 1 to 4, alkoxy groups whose carbon number is 1 to 4, alicyclic hydrocarbon groups whose carbon number is 3 to 6 and aromatic hydrocarbon groups whose carbon number is 6 to 10, and R^{18} represents a species selected from hydrogen, alkyl groups whose carbon number is 1 to 4, alkoxy groups whose carbon number is 1 to 4, alicyclic hydrocarbon groups whose carbon number is 3 to 6, aromatic hydrocarbon groups whose carbon number is 6 to 10, halogen atoms, ester groups, acyl groups and a nitro group.)

[0050] Furthermore, as a high level of dispersion stability is to be achieved, the acryl copolymer used in the invention is more preferred to be copolymerized from a (meth)acryl monomer having in a side chain a long-chain alkyl group which is represented by the formula (F) below.

[Chem. 15]



(In the formula, R^{19} represents a hydrogen atom or a methyl group, R^{20} represents a hydrogen atom or an alkyl group whose carbon atom number 1 to 20, and R^{21} represents an alkyl group whose carbon atom number 2 to 40.)

[0051] In the aforementioned formula (F), R^{19} is a hydrogen atom or a methyl group, and when R^{19} is hydrogen, an acryl unit is formed, and when R^{19} is a methyl group, a methacryl unit is formed. R^{20} is hydrogen or an alkyl group whose carbon number is 1 to 20, and is preferably hydrogen or an alkyl group whose carbon number is 2 to 6. R^{21} is an alkyl group whose carbon atom number 2 to 40, and is preferably an alkyl group

whose carbon number is 2 to 18. In the invention, this acryl monomer is defined to be a structure that has in a side chain a carboxylic acid ester.

[0052] As for the unsaturated monomer containing a carboxylic acid ester which is represented by the formula (F), a total of the carbon atom numbers of R^{20} and R^{21} is preferred to be greater than or equal to 4, and more preferred to be 4 to 24. Incidentally, when R^{20} is hydrogen, it suffices that R^{21} is an alkyl group whose carbon number is greater than or equal to 4. By making the total of the carbon numbers of R^{20} and R^{21} greater than or equal to 4, the dispersion stability of the coloring material can be further improved.

[0053] As the unsaturated monomer containing a carboxylic acid ester which is represented by the formula (F), 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate, etc. can be cited as example; however, the unsaturated monomer containing a carboxylic acid ester is not particularly limited. These acryl monomers may be used singly or may also be used in a mixture of two or more species.

[0054] In the invention, the structure having in a side chain a carboxylic acid ester can be introduced by copolymerizing a long-chain alkyl group-containing unsaturated monomer. As the long-chain alkyl group-containing unsaturated monomer, octyl acrylate, octyl methacrylate, lauryl acrylate, lauryl methacrylate, stearyl acrylate, stearyl methacrylate, dodecyl acrylate, dodecyl methacrylate, etc., can be cited as examples. In particular, unsaturated monomers having in a side chain a carboxylic acid ester which are represented by the aforementioned formula (F) have tendency of manifesting a higher level of dispersion stability, and therefore are particularly preferable.

[0055] The acryl copolymer of the invention can be copolymerized by using an arbitrary (meth)acrylic acid ester as a monomer according to needs in addition to the structural unit cited above. Concretely, there can be cited, as examples, acrylic acid esters and methacrylic acid esters, including methyl acrylate, ethyl acrylate, propyl acrylate, isopropyl acrylate, n-butyl acrylate, isobutyl acrylate, t-butyl acrylate, cyclohexyl acrylate, isobornyl acrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylate, isopropyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, t-butyl

methacrylate, cyclohexyl methacrylate, isobornyl methacrylate, etc., (fluoro)alkyl ester monomers thereof. However, the aforementioned arbitrary (meth)acrylic acid ester is not limited to these.

[0056] In the acryl copolymer used in the invention, it is important that the acid value and the base value be in appropriate ranges. It is essential that the base value be 5 to 70 mmol/100 g. Preferably, it is desired that copolymerization be performed so that the base value is 10 to 30 mmol/100 g. If the base value is below this range, the pigment dispersion stability deteriorates. If the base value is above this range, the development property deteriorates. The base value can be caused to be in a predetermined range by adjusting the composition ratio of the constitutional units of the acryl copolymer and, particularly, the composition ratios of the structural units of the formulas (B) and (C). Incidentally, the base value of the acryl copolymer is defined to be the mole number of perchloric acid needed in order to neutralize 100 g of the acryl copolymer (unit: mmol/100 g).

[0057] It is essential that the acid value of the acryl copolymer be 50 to 120 mgKOH/g. Preferably, it is desirable that the acryl copolymer be copolymerized so that the acid value thereof is 50 to 100 mgKOH/g. If the upper limit of the range is exceeded, a tendency of deterioration of the dispersion stability is observed. If the lower limit thereof is exceeded, a tendency of the alkaline development becoming difficult is observed. The acid value thereof can be kept within a predetermined range by adjusting the composition ratio of the constitutional units of the acryl copolymer. Incidentally, the acid value of the acryl copolymer is defined to be mg amount of KOH of potassium hydroxide (mgKOH) needed to neutralize 1 g of the acryl copolymer (unit: mgKOH/g).

[0058] In the invention, the weight-average molecular weight (M_w) of the acryl copolymer is 5,000 to 30,000, and preferably 5,000 to 20,000. If the weight-average molecular weight is less than 5,000, sufficient steric hindrance cannot be formed, and dispersion destabilizes due to interaction between coloring materials. On the other hand, if the weight-average molecular weight is greater than 30,000, there occurs a problem of

decline of resin adsorption probability per coloring material unit leading to destabilization of dispersion or to deterioration of the development property. Incidentally, the weight-average molecular weight (Mw) of the acryl copolymer is obtained by performing measurement in gel permeation chromatography using tetrahydrofuran as a carrier and converting the measured value by using a calibration curve with standard polystyrene.

[0059] In the acryl copolymer used in the invention, the structural units represented by the formulas (B), (C), (D1), (E1), (E2) and (F) and, furthermore, other arbitrary (meth)acrylic acid ester units can be obtained in forms of a random copolymer, a block copolymer, etc., by an ordinary radical polymerization reaction such as solution polymerization, emulsion polymerization or bulk polymerization. Particularly, the form of a random copolymer is preferable. Furthermore, the (meth)acryl unit represented by the formula (A) can be introduced by an ordinary method in which a side chain functional group of the acryl copolymer obtained as described above is subjected to the addition reaction with a monomer that has a functional group capable of reacting with the side chain functional group.

[0060] The organic solvent used in the coloring material dispersion liquid of the invention is not particularly limited. Concretely, at least one species selected from aliphatic hydrocarbons, carboxylic acid esters, ketones, ethers and alcohols can be cited. In particular, at least one species selected from carboxylic acid esters, ketones and ethers can be used. As carboxylic acid esters that can be preferably used, esters made up of a saturated aliphatic carboxylic acid and a saturated alcohol can be cited.

[0061] As concrete esters, there can be cited benzyl acetate, ethyl benzoate, γ -butyrolactone, methyl benzoate, diethyl malonate, 2-ethylhexyl acetate, 2-butoxyethyl acetate, 3-methoxy-3-methyl-butyl acetate, oxalic acid diethyl, ethyl acetoacetate, cyclohexyl acetate, 3-methoxy-butyl acetate, methyl acetoacetate, ethyl-3-ethoxy propionate, 2-ethylbutyl acetate, isopentyl propionate, propylene glycol monomethyl ether propionate, propylene glycol monoethyl ether acetate, pentyl acetate, propylene glycol monomethyl ether acetate, etc.; however, the esters are not limited to these.

[0062] Among these organic solvents, particularly preferred are acetic acid ester-base

or propionic acid ester-base 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.

[0063] Furthermore, as organic solvents other than the aforementioned ones, aliphatic ethers, such as propylene glycol derivatives, including propylene glycol monomethyl ether, propylene glycol monoethyl ether, propylene glycol tertiary butyl ether, dipropylene glycol monomethyl ether, etc., aliphatic esters other than the aforementioned ones, for example, ethyl acetate, butyl acetate and isopentyl acetate, aliphatic alcohols, such as butanol, 3-methyl-2-butanol, 3-methyl-3-methoxy butanol, etc., ketones, such as cyclopentanone, cyclohexanone, etc., organic solvents such as xylene, ethyl benzene, solvent naphtha, etc. can also be used together with an organic solvent as mentioned above.

[0064] In the coloring material dispersion liquid of the invention, as a coloring material, any one of organic pigments, inorganic pigments and dyes can be suitably used.

[0065] As the organic pigments, there can be cited diketopyrrolo pyrrole-based pigments, azo-based pigments, such as, azo, disazo, or polyazo pigments, etc., phthalocyanine system pigments, such as copper phthalocyanine, halogenated copper phthalocyanine, non-metallo phthalocyanine, etc., anthraquinone-based pigments, such as aminoanthraquinone, diaminodianthraquinone, anthrapyrimidine, flavanthrone, anthanthrone, indanthrone, pyranthrone, violanthrone, etc., quinacridone-based pigments, dioxazine-based pigments, perinone-based pigments, perylene-based pigments, thioindigo-based pigments, isoindoline-based pigments, isoindolinone-based pigments, quinophthalone-based pigments, threne-based pigments, metal complex-based pigments, etc.

[0066] As the inorganic pigments, there can be cited titanium oxide, zinc white, zinc sulfide, white lead, calcium carbonate, precipitated barium sulfate, white carbon, alumina white, kaolinite clay, talc, bentonite, black iron oxide, cadmium red, red oxide, molybdenum red, molybdate orange, chrome vermilion, lead yellow, cadmium yellow, yellow iron oxide, titanium yellow, chromic oxide, viridian, titanium cobalt green, cobalt

green, cobalt chrome green, victoria green, ultramarine, iron blue, cobalt blue, cerulean blue, cobalt silica blue, cobalt zinc silica blue, manganese violet, cobalt violet, etc.

[0067] As the dyes, for example, azo dye, anthraquinone dye, condensed polycyclic aromatic carbonyl dye, indigoid dye, carbonium dye, phthalocyanine dye, methine, polymethine dye, etc. are cited.

[0068] Where concrete examples of representative pigments and dyes are indicated by color index (CI) number, pigments or dyes as follows are preferably used; however, neither the pigment nor the dye is limited to these.

[0069] As examples of red pigment, Pigment Red (hereinafter, abbreviated as PR) 9, PR 48, PR 97, PR 122, PR 123, PR 144, PR 149, PR 166, PR 168, PR 177, PR 179, PR 180, PR 192, PR 209, PR 215, PR 216, PR 217, PR 220, PR 223, PR 224, PR 226, PR 227, PR 228, PR 240, PR 254, etc. are used.

[0070] As examples of orange color pigment, Pigment Orange (hereinafter, abbreviated as PO) 13, PO 36, PO 38, PO 43, PO 51, PO 55, PO 59, PO 61, PO 64, PO 65, PO 71, etc. are used.

[0071] As examples of yellow pigment, Pigment Yellow (hereinafter, abbreviated as PY) PY 12, PY 13, PY 17, PY 20, PY 24, PY 83, PY 86, PY 93, PY 95, PY 109, PY 110, PY 117, PY 125, PY 129, PY 137, PY 138, PY 139, PY 147, PY 148, PY 150, PY 153, PY 154, PY 166, PY 168, PY 185, etc. are used.

[0072] Furthermore, as examples of violet pigment, Pigment Violet (hereinafter, abbreviated as PV) 19, PV 23, PV 29, PV 30, PV 32, PV 37, PV 40, PV 50, etc. are used.

[0073] Furthermore, as examples of blue pigment, Pigment Blue (hereinafter, abbreviated as PB) 15, PB 15:3, PB 15:4, PB 15:6, PB 22, PB 60, PB 64, etc. are used.

[0074] Furthermore, as examples of green pigment, Pigment Green (hereinafter, abbreviated as PG) 7, PG 10, PG 36, PG 58, etc. are used.

[0075] As examples of black pigment, pigments from a range of black organic pigments, mixed-color organic pigments, inorganic pigments, etc. can be employed. As black organic pigments, there are cited carbon black, perylene black, aniline black, etc.; as mixed-color organic pigments, there are cited pigments obtained mixing at least two or

more species of pigments selected from red, blue, green, violet, yellow, magenta, cyan, etc., so as to make a pseudo black color; and, as inorganic pigments, there are cited graphite, metal fine particles of titanium, copper, iron, manganese, cobalt, chrome, nickel, zinc, calcium, silver, etc., metal oxides, composite oxides, metal sulfates, metal nitrides, metal oxynitrides, etc. These may be employed singly in a single species, or may also be employed in a mixture of two or more species. In particular, carbon black and titanium nitrides are preferably employed because of having a high light blocking characteristic.

[0076] Furthermore, as examples of the white pigment, there are cited titanium dioxide, barium carbonate, zirconium oxide, calcium carbonate, barium sulfate, alumina white, silicon dioxide, etc.

[0077] As examples of dyes, there are cited, for example: C.I. Direct Red 2, 4, 9, 23, 26, 28, 31, 39, 62, 63, 72, 75, 76, 79, 80, 81, 83, 84, 89, 92, 95, 111, 173, 184, 207, 211, 212, 214, 218, 221, 223, 224, 225, 226, 227, 232, 233, 240, 241, 242, 243 and 247; C.I. Acid Red 35, 42, 51, 52, 57, 62, 80, 82, 111, 114, 118, 119, 127, 128, 131, 143, 145, 151, 154, 157, 158, 211, 249, 254, 257, 261, 263, 266, 289, 299, 301, 305, 319, 336, 337, 361, 396 and 397; C.I. Reactive Red 3, 13, 17, 19, 21, 22, 23, 24, 29, 35, 37, 40, 41, 43, 45, 49 and 55; C.I. Basic Red 12, 13, 14, 15, 18, 22, 23, 24, 25, 27, 29, 35, 36, 38, 39, 45 and 46; C.I. Direct Violet 7, 9, 47, 48, 51, 66, 90, 93, 94, 95, 98, 100 and 101; C.I. Acid Violet 5, 9, 11, 34, 43, 47, 48, 51, 75, 90, 103 and 126; C.I. Reactive Violet 1, 3, 4, 5, 6, 7, 8, 9, 16, 17, 22, 23, 24, 26, 27, 33 and 34; C.I. Basic Violet 1, 2, 3, 7, 10, 15, 16, 20, 21, 25, 27, 28, 35, 37, 39, 40 and 48; C.I. Direct Yellow 8, 9, 11, 12, 27, 28, 29, 33, 35, 39, 41, 44, 50, 53, 58, 59, 68, 87, 93, 95, 96, 98, 100, 106, 108, 109, 110, 130, 142, 144, 161 and 163; C.I. Acid Yellow 17, 19, 23, 25, 39, 40, 42, 44, 49, 50, 61, 64, 76, 79, 110, 127, 135, 143, 151, 159, 169, 174, 190, 195, 196, 197, 199, 218, 219, 222 and 227; C.I. Reactive Yellow 2, 3, 13, 14, 15, 17, 18, 23, 24, 25, 26, 27, 29, 35, 37, 41 and 42; C.I. Basic Yellow 1, 2, 4, 11, 13, 14, 15, 19, 21, 23, 24, 25, 28, 29, 32, 36, 39 and 40; C.I. Acid Green 16; C.I. Acid Blue 9, 45, 80, 83, 90 and 185; C.I. Basic Orange 21 and 23; etc.

[0078] In the coloring material dispersion liquid of the invention, it is more preferable

to add a high-molecular dispersing agent, in order to homogeneously and stably disperse the coloring material in the resin solution. As the high-molecular dispersing agent, there are cited polyester-based high-molecular dispersing agents, acryl-based high-molecular dispersing agents, polyurethane-based high-molecular dispersing agents, polyallylamine-based high-molecular dispersing agents, carbodiimide-based dispersing agents, etc. These high-molecular dispersing agents are used selectively as appropriate according to the kind of the coloring material.

[0079] Among the high-molecular dispersing agents, there exist various dispersing agents, including dispersing agents having only amine values, dispersing agents having only acid values, dispersing agents having amine values and acid values, and dispersing agents having neither an amine value nor an acid value. However, in order to make the effects of the invention conspicuous, it is more preferable to employ a dispersing agent having an amine value, and more preferably a high-molecular dispersing agent having only an amine value is preferable.

[0080] As concrete examples of the dispersing agent having only an amine value, there are cited: DISPERBYK-102, DISPERBYK-160, DISPERBYK-161, DISPERBYK-162, DISPERBYK-2163, DISPERBYK-2164, DISPERBYK-166, DISPERBYK-167, DISPERBYK-168, DISPERBYK-2000, DISPERBYK-2050, DISPERBYK-2150, DISPERBYK-2155, DISPERBYK LPN-6919, DISPERBYK LPN-21116, DISPERBYK LPN-21234, DISPERBYK-9075 and DISPERBYK-9077 (which are all made by BYK Chemie company); EFKA 4015, EFKA 4020, EFKA 4046, EFKA 4047, EFKA 4050, EFKA 4055, EFKA 4060, EFKA 4080, EFKA 4300, EFKA 4330, EFKA 4340, EFKA 4400, EFKA 4401, EFKA 4402, EFKA 4403 and EFKA 4800 (which are all made by BASF company); AJISPER PB 711 (made by Ajinomoto Fine-Techno Co., Inc.); etc. However, the dispersing agent having only an amine value is not limited to these.

[0081] As for the dispersing agent having only an amine value, it is particularly more preferable to employ a high-molecular dispersing agent having at least a tertiary amino group; as concrete examples thereof, DISPERBYK LPN-6919, DISPERBYK LPN-21116,

etc., are cited.

[0082] As concrete examples of the high-molecular dispersing agent having an amine value and an acid value, there can be cited: DISPERBYK-142, DISPERBYK-145, DISPERBYK-2001, DISPERBYK-2010, DISPERBYK-2020, DISPERBYK-2025, DISPERBYK-9076, Anti-Terra-205 (which are all made by BYK Chemie company); SOLSPERSE 24000 (made by The Lubrizol Corporation); AJISPER PB 821, AJISPER PB 880, AJISPER PB 881 (which are all made by Ajinomoto Fine-Techno Co., Inc.); etc.

[0083] These high-molecular dispersing agents may be employed singly or may also be employed in a combination of two or more species. These high-molecular dispersing agents do not have photosensitivity, and therefore adding it in a large amount induces a concern of deteriorating the photosensitive performance of the photosensitive coloring resin composition intended; hence, it is desirable to realize a proper addition amount of the agent factoring in the dispersion stability and the photosensitive performance.

Addition of 1 to 50 (mass%) thereof to the coloring material and more preferably addition of 3 to 30 (mas%) thereof to it will have an effect of highly stabilizing the dispersion without deteriorating the photosensitive performance, and there are even more preferable.

[0084] In the coloring material dispersion liquid of the invention, the weight composition ratio of coloring material component/resin component is preferred to be within the range of 90/10 to 20/80, and more preferably 90/10 to 40/60. The resin component herein is a total of the high-molecular dispersing agent and the like in addition to the acryl copolymer. If the amount of the resin component is excessively small, the dispersion stability of the coloring material becomes no good. The amount of the coloring material component being excessively small, conversely, makes it difficult to form a coating film that has high coloring power at the time of formation of a coloring coating film through the use of the coloring material dispersion liquid, and therefore is not preferable.

[0085] The solid content concentration of the resin component and the coloring material component combined in the coloring material dispersion liquid of the invention is preferred to be greater than or equal to 2 mass% and less than or equal to 60 mass%,

and further preferred to be greater than or equal to 5 mass% and less than or equal to 30 mass%, from the viewpoint of dispersion stability and productivity.

[0086] As for the production method for the coloring material dispersion liquid of the invention, there are no specific restrictions thereon; however, a method in which a coloring material is dispersed in an acryl copolymer solution by using a dispersion machine is generally performed.

[0087] As the dispersion machine that disperses the coloring material, various methods can be adopted, such as a ball mill, a sand grinder, a three-roll mill, a high-speed impact mill, etc.; however, a bead mill is preferred, from the standpoint of dispersion efficiency and making finer dispersion. As the bead mill, a Co-ball mill, a basket mill, a pin mill, a Dino mill, etc. can be employed. As beads for the bead mill, it is preferable to employ titania beads, zirconia beads, zircon beads, etc.

[0088] As the bead diameter employed for dispersion, a diameter greater than or equal to 0.01 mm and less than or equal to 5.0 mm is preferable, and more preferable is a diameter greater than or equal to 0.03 mm and less than or equal to 1.0 mm. In the case where the primary particle diameter of the coloring material and the particle diameter of secondary particles formed by aggregation of primary particles are small, it is preferable to employ small dispersion beads that are larger than or equal to 0.03 mm and smaller than or equal to 0.10 mm. In this case, it is preferable to perform dispersion by using a bead mill that has a separator based on a centrifugal separation method which is capable of separating small dispersion beads and a dispersion liquid. On the other hand, to disperse a coloring material that contains coarse and large particles of approximately a sub-micron order in size, the use of dispersion beads larger than or equal to 0.10 mm makes it possible to provide a sufficient pulverization force and therefore finely disperse the pigment, and hence is preferable.

[0089] The photosensitive coloring resin composition in which the coloring material dispersion liquid of the invention is employed will be illustrated with examples hereinafter, but is not limited to these examples.

[0090] The photosensitive coloring resin composition of the invention is constructed

by adding into the coloring material dispersion liquid of the invention at least an alkali-soluble polymer, a reactive monomer and a photopolymerization initiator. As for the quantitative ratio of these materials, usually, a weight composition ratio between the alkali-soluble polymer and the reactive monomer is 10/90 to 90/10, and the addition amount of the photopolymerization initiator is about 1 to 20 wt% relative to the sum of the weights of the polymer and the monomer. Herein, as the weight of the alkali-soluble polymer, the total sum of the weight of the newly added alkali-soluble polymer and, in addition, the weight of the acryl copolymer contained in the coloring material dispersion liquid is employed.

[0091] As the alkali-soluble polymer of the photosensitive coloring resin composition of the invention, the acryl copolymer employed in the coloring material dispersion liquid may be employed or the new alkali-soluble polymer may also be employed. The alkali-soluble polymer newly employed will be described in detail hereinafter.

[0092] As the alkali-soluble polymer, an alkali-soluble polymer having a carboxyl group is preferable, and a copolymer of an unsaturated carboxylic acid and an ethylenic unsaturated compound can be preferably employed. As examples of the unsaturated carboxylic acid, there are cited, for example: monocarboxylic acids, including acrylic acid, methacrylic acid, crotonic acid, vinyl acetate, etc.; dicarboxylic acids, including itaconic acid, maleic acid, fumaric acid, etc., and acid anhydrides thereof; polyvalent carboxylic acid monoesters, including mono(2-(meth)acryloyloxyethyl) phthalate, etc.; etc. Particularly, an acryl-based polymer that contains a constitutional unit derived from (meth)acrylic acid is preferable. Furthermore, an acryl-based polymer obtained by reacting a compound that contains an ethylenic unsaturated group and an epoxy group with the carboxylic acid contained in a constitutional unit, if employed, will better the sensitivity in exposure and development, and therefore can be preferably employed. As the ethylenic unsaturated group, an acryl group and a methacryl group are preferable.

[0093] These may be employed singly, but may also be employed in a combination with other polymerizable ethylenic unsaturated compound. As the polymerizable ethylenic unsaturated compound, there can be concretely cited: unsaturated carboxylic

acid alkyl esters, including 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-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, benzyl methacrylate, etc.; aromatic vinyl compounds, including styrene, p-methylstyrene, o-methylstyrene, m-methylstyrene, α -methylstyrene, etc.; (crosslinked) cyclic hydrocarbon groups, including tricyclodecanyl (meth)acrylate, etc.; unsaturated carboxylic acid aminoalkyl esters, including aminoethyl acrylate, etc.; unsaturated carboxylic acid glycidyl esters, including glycidyl acrylate, glycidyl methacrylate, etc.; carboxylic acid vinyl esters, including vinyl acetate, propionic acid vinyl, etc.; vinyl cyanide compounds, including acrylonitrile, methacrylonitrile, α -chloroacrylonitrile, etc.; aliphatic conjugated dienes, including 1,3-butadiene, isoprene, etc.; and polystyrene, polymethyl acrylate, polymethyl methacrylate, polybutyl acrylate, polybutyl methacrylate, etc. each of which has on a terminal an acryloyl group or a methacryloyl group. However, the polymerizable ethylenic unsaturated compound is not limited to these.

[0094] Particularly, acryl-based polymers that contain (meth)acrylic acid and benzyl (meth)acrylate are particularly preferable from the viewpoint of dispersion stability and pattern workability.

[0095] Furthermore, other than the acryl-based polymers obtained by reacting a compound that contains an ethylenic unsaturated group and an epoxy group with (meth)acrylic acid that is included in above-mentioned constitutional units, an acryl-based polymer having in a side chain an ethylenic unsaturated group can be preferably employed. As concrete examples thereof, copolymers mentioned in Japanese Patent No. 3120476 and Japanese Unexamined Patent Publication (Kokai) No. 8-262221, a photo-curing resin "Cyclomer (registered trademark)P" (Daicel Chemical Industries, Ltd.), which is a commercially sold acryl-based polymer, alkali-soluble cardo resin, etc. are cited.

[0096] The weight-average molecular weight (Mw) of the alkali-soluble polymer is preferred to be five thousand to forty thousand (which is obtained by performing measurement in gel permeation chromatography using tetrahydrofuran as a carrier and converting the measured value by using a calibration curve with standard polystyrene). Furthermore, such polymers whose average molecular weight is eight thousand to forty thousand and whose acid value is 60 to 150 (mgKOH/g) are most preferable from the viewpoints of photosensitive characteristic, the solubility in ester-based solvents, the solubility to alkaline developer liquids, and residue reduction.

[0097] As the reactive monomer of the photosensitive coloring resin composition of the invention, a multifunctional or monofunctional acryl-based monomer or oligomer can be employed. In particular, it is preferable that a multifunctional monomer be contained. As multifunctional monomers, there are cited, for example, bisphenol A diglycidyl ether (meth)acrylate, poly(meth)acrylate carbamate, modified bisphenol A epoxy (meth)acrylate, adipic acid 1,6-hexanediol (meth)acrylic acid ester, phthalic anhydride propylene oxide (meth)acrylic acid ester, trimellitic acid diethylene glycol (meth)acrylic acid ester, rosin-modified epoxy di(meth)acrylate, alkyd-modified (meth)acrylate, fluorene diacrylate-based oligomer as mentioned in Japanese Patent No. 3621533 or Japanese Unexamined Patent Publication (Kokai) No. 8-278630, tripropylene glycol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, bisphenol A diglycidyl ether di(meth)acrylate, trimethylolpropane tri(meth)acrylate, pentaerythritol tri(meth)acrylate, triacrylformal, pentaerythritol tetra(meth)acrylate and its acid-modified products, dipentaerythritol hexa(meth)acrylate and its acid-modified products, dipentaerythritol penta(meth)acrylate and its acid-modified products, 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, 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, bisphenoxy ethanol fluorene diacrylate, bisphenoxy ethanol fluorene dimethacrylate, bisresol fluorene diacrylate, bisresol fluorene dimethacrylate, etc. These can be employed singly or in mixture.

[0098] The sensitivity of the resist and the characteristic of work can be controlled by selection and combination from these multifunctional monomer or oligomers.

Particularly, in order to increase the sensitivity, it is desirable to use a compound whose functional groups are greater than or equal to 3 in number and preferably greater than or equal to 5 in number. Particularly, dipentaerythritol hexa(meth)acrylate, dipentaerythritol penta(meth)acrylate and acid-modified products thereof are preferable. Furthermore, unsaturated group-containing alkali-soluble monomers obtained by reacting a polybasic acid carboxylic acid and its acid anhydride with a reaction product of a methacrylic acid and an epoxy compound having two glycidyl ether groups are also preferably employed from the viewpoint of development property and workability. Furthermore, a combined use of a (meth)acrylate having a fluorene ring which contains in its molecule many aromatic rings and is high in water repellency makes it possible to control the pattern to a desirable shape at the time of development, and is therefore preferable.

[0099] As for the photopolymerization initiator of the photosensitive coloring resin composition of the invention, there are no specific limitations. However, preferably, it is preferable that the photopolymerization initiator be a photo-radical polymerization initiating agent and, in particular, it is more preferable that alkyl phenone-based and/or oxime ester-based photopolymerization initiator be contained.

[0100] As the alkyl phenone-based photopolymerization initiator, α -aminoalkyl phenone-based or α -hydroxyalkyl phenone-based ones are cited; particularly, α -aminoalkyl phenone-based ones are preferable from the viewpoint of high sensitivity. For example, 2,2-diethoxyacetophenone, 2-methyl-1-(4-methylthiophenyl)-2-morpholinopropane-1-one,

2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone, which is Ciba Specialty Chemicals Corp. "IRGACURE (registered trademark)" 369,
 2-(dimethylamino)-2-[(4-methylphenyl)methyl]-1-[4-(4-morpholinyl)phenyl]-1-butanone, which is Ciba Specialty Chemicals Corp. "IRGACURE (registered trademark)" 379,
 1-hydroxycyclohexyl phenyl ketone, 2-hydroxy-2-methyl-1-phenyl propane-1-one, etc. are cited.

[0101] As concrete examples of the oxime ester-based photopolymerization initiator, there are cited 1,2-octanedione, 1-[4-(phenylthio)-2-(O-benzoyloxime)], which is Ciba Specialty Chemicals Corp. "IRGACURE (registered trademark)" OXE01, ethanone, 1-[9-ethyl-6-(2-methylbenzoyl)-9H-carbazol-3-yl]-, 1-(O-acetyloxime), which is Ciba Specialty Chemicals Corp. "IRGACURE (registered trademark)" OXE02, "ADEKA (registered trademark) OPTOMER" N-1818 and N-1919, and "ADEKA KLUSE" NCI-831 made by Asahi Denka Kogyo K.K., etc.

[0102] Furthermore, in addition to these photopolymerization initiators, it is also possible to employ a combined use of a publicly known photopolymerization initiator, such as benzophenone-based compounds, oxanthone-based compounds, imidazole-based compounds, benzothiazole-based compounds, benzoxazole-based compounds, carbazol-based compounds, triazine-based compounds, phosphorus-based compounds, or inorganic photopolymerization initiators, including titanates and the like, etc. For example, benzophenone, N,N'-tetraethyl-4,4'-diaminobenzophenone, 4-methoxy-4'-dimethylamino benzophenone, benzoin, benzoin methyl ether, benzoin isobutyl ether, benzyl dimethyl ketal, α -hydroxyisobutyl phenone, thioxanthone, 2-chlorothioxanthone, t-butyl anthraquinone, 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-diphenyl imidazole dimer, 2-mercaptobenzothiazole, 2-mercaptobenzoxazole, 4-(p-methoxyphenyl)-2,6-di-(trichloromethyl)-s-triazine, etc. are cited.

[0103] As organic solvents that are preferably employed in the photosensitive

coloring resin composition of the invention, there is no particular limitation, and esters, aliphatic alcohols, ketones, etc., can be used.

[0104] As concrete esters, benzyl acetate (a boiling point of 214°C), ethyl benzoate (a boiling point of 213°C), γ -butyrolactone (a boiling point of 204°C), methyl benzoate (a boiling point of 200°C), diethyl malate (a boiling point of 199°C), 2-ethylhexyl acetate (a boiling point of 199°C), 2-butoxyethyl acetate (a boiling point of 192°C), 3-methoxy-3-methyl-butyl acetate (a boiling point of 188°C), diethyl oxalate (a boiling point of 185°C), ethyl acetoacetate (a boiling point of 181°C), cyclohexyl acetate (a boiling point of 174°C), 3-methoxy-butyl acetate (a boiling point of 173°C), methyl acetoacetate (a boiling point of 172°C), ethyl-3-ethoxy propionate (a boiling point of 170°C), 2-ethylbutyl acetate (a boiling point of 162°C), isopentyl propionate (a boiling point of 160°C), propylene glycol monomethyl ether propionate (a boiling point of 160°C), propylene glycol monoethyl ether acetate (a boiling point of 158°C), pentyl acetate (a boiling point of 150°C), propylene glycol monomethyl ether acetate (a boiling point of 146°C), etc. are cited; however, the esters are not limited to these.

[0105] Among these solvents, 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, which are acetic acid ester-based or propionic acid ester-based solvents, are particularly preferable.

[0106] Furthermore, as solvents other than the aforementioned ones, it is also possible to adopt a combined use with a solvent, such as, aliphatic ethers, such as propylene glycol derivatives, including propylene glycol monomethyl ether (a boiling point of 120°C), propylene glycol monoethyl ether (a boiling point of 133°C), propylene glycol tertiary butyl ether (a boiling point of 153°C), dipropylene glycol monomethyl ether (a boiling point of 188°C), etc., aliphatic esters other than the aforementioned ones, for example, ethyl acetate (a boiling point of 77°C), butyl acetate (a boiling point of 126°C) and isopentyl acetate (a boiling point of 142°C), or aliphatic alcohols, including butanol (a boiling point of 118°C), 3-methyl-2-butanol (a boiling point of 112°C), 3-methyl-3-methoxy butanol (a boiling point of 174°C), etc., ketones, including

cyclopentanone, cyclohexanone, etc., solvents, such as xylene (a boiling point of 144°C), ethyl benzene (a boiling point of 136°C), solvent naphtha (petroleum fraction: a boiling point of 165 to 178°C), etc.

[0107] Furthermore, since the coating with a die coating apparatus is becoming a mainstream with the size increases of substrates, it is preferable to construct the solvent from a mixed solvent containing two or more components as appropriate volatility and drying property are to be realized. In the case where all the solvents constituting the mixed solvent have boiling points lower than or equal to 150°C, many problems occur, including a problem that uniformity of the film thickness cannot be obtained, a problem that the film thickness at a coating-completed portion becomes thick, and a problem that aggregate of pigment forms on a nozzle piece portion for discharging a coating liquid from a slit, and results in occurrence of lines on the coating film. On the other hand, in the case where the mixed solvent contain a large amount of a solvent whose boiling point is higher than or equal to 200°C, the coating film surface becomes sticky, and causes sticking. Therefore, a mixed solvent containing 30 to 75 mass% of a solvent whose boiling point is 150°C or higher and 200°C or lower is desirable.

[0108] In the photosensitive coloring resin composition of the invention, as the adhesion property between the coating film and a base substrate is to be improved, it is preferable to add a close adhesion improvement agent into the coloring resin composition. For this, a silane coupling agent is preferably used. As for the silane coupling agent, there are no specific restrictions, and silane coupling agents having a functional group, such as a vinyl group, an epoxy group, a styryl group, methacryloxy group, an acryloxy group, an amino group, etc., are cited. However, the silane coupling agent is not limited to these. Concretely, 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-dimethyl-butylidene)propylamine,
 3-mercaptopropyltrimethoxysilane, 3-ureidopropyltriethoxysilane,
 3-isocyanatepropyltriethoxysilane, p-styryltrimethoxysilane, etc. are preferable.

[0109] The amount of the close adhesion improvement agent added is preferred to be 1 to 15 mass%, and more preferred to be 2 to 10 mass%, relative to the total solid component amount of the coloring resin composition, that is, the total sum of the coloring material, the acryl copolymer, the alkali-soluble polymer and the reactive monomer. If the addition amount thereof is less than 1 mass%, the adhesion property improvement effect is not sufficient. If the addition amount thereof is greater than 15 mass%, fine patterns are depleted in an alkaline development, and therefore the resolution declines.

[0110] Furthermore, in the photosensitive coloring resin composition of the invention, a surface active agent can be added for the purpose of prevention of Benard cells or smoothness of a coloring coating and coating property. The amount of the surface active agent added is usually 0.001 to 10 mass% and preferably 0.01 to 1 mass% relative to the pigment. If the addition amount thereof is excessively small, there is no effect of prevention of Benard cells, smoothness of a coloring coating and the coating property. If the addition amount thereof is excessively large, the coating film physical property sometimes becomes no good.

[0111] As concrete examples of the surface active agent, there are cited: anionic surface active agents, including ammonium lauryl sulfate, polyoxyethylenealkyl ether sulfate triethanol amine, etc.; cationic surface active agents, including stearylamine acetate, lauryl trimethylammonium chloride, etc.; amphoteric surface active agents, including lauryl dimethylamine oxide, lauryl carboxymethyl hydroxyethyl imidazolium betaine, etc.; nonionic surface active agents, including polyoxyethylene lauryl ether, polyoxyethylene stearyl ether, sorbitan monostearate, etc.; silicone-based surface active agents that have polydimethyl siloxane or the like as a main skeleton; fluorine-based

surface active agents; etc. In the invention, the surface active agent is not limited to these agents, and one species or two or more species of surface active agents can be employed.

[0112] In the photosensitive coloring resin composition of the invention, the weight composition ratio of coloring material component/resin component is preferred to be in the range of 80/20 to 10/90, in order to obtain a coating film that has a sufficient coloring power. Herein, the resin component is defined as being a total of additives that include the reactive monomers or oligomers, the photopolymerization initiator, the high-molecular dispersing agent, etc., in addition to the acryl copolymer employed in the coloring material dispersion liquid and the alkali-soluble polymer added into the coloring resin composition.

[0113] In the photosensitive coloring resin composition of the invention, the solid content concentration combining the resin component and the coloring material component is preferred to be greater than or equal to 2% and less than or equal to 60%, and is further preferred to be greater than or equal to 5% and less than or equal to 30%, from the viewpoint of coating property and drying property.

[EXAMPLES]

[0114] The invention will be further described in detail hereinafter with reference to Examples and Comparative Examples; however, the invention is not limited to the following Examples.

[0115] <EVALUATION METHOD>

"ACID VALUE"

The amount (mg) of potassium hydroxide needed to neutralize 1 g of acryl copolymer was defined as an acid value (unit: mgKOH/g).

[0116] "BASE VALUE"

The mole number of perchloric acid needed to neutralize 100 g of acryl copolymer was defined as a base value (unit: mmol/100 g).

[0117] "MOLECULAR WEIGHT"

The molecular weight is defined as a value of weight-average molecular weight

(Mw) measured with tetrahydrofuran employed as a carrier and polystyrene employed as a molecular weight standard, by using a gel permeation chromatography (GPC)

“HLC-8220GPC” (a tester apparatus of TOSOH CORP.).

[0118] “VISCOSITY”

The value obtained at 100 rpm on a viscometer (RE105L made by Toki Sangyo Co., Ltd.) set at a temperature of $25.0 \pm 0.2^{\circ}\text{C}$ is defined as a value of viscosity.

[0119] “DISPERSION STABILITY”

The state of dispersion was comprehensively evaluated as stated below, on the basis of the initial viscosity of the coloring material dispersion liquid, and the change in viscosity one week after, that is, the percentage of the increase in the viscosity one week after relative to the initial viscosity (viscosity increase, whose unit is %). The time-dependent viscosity increase is desired to be small. However, in some cases, the viscosity increases due to interaction between finely dispersed pigments. Therefore, the state of dispersion was evaluated as stated below, with Δ being a tolerance standard.

○: The state of dispersion is very good (the viscosity increase one week after the manufacture is within 50%).

Δ : The state of dispersion is good (the viscosity increase one week after the manufacture is beyond 50% but within 100%).

×: The state of dispersion is unstable (the viscosity increase one week after the manufacture is greater than 100%).

[0120] “DEVELOPMENT PROPERTY”

The dissolution time of an unexposed portion of each developed coating film in a 0.045% potassium hydroxide aqueous solution was evaluated as follows, with Δ being a tolerance standard, from the viewpoint of industrial use.

○: The development property is very good (dissolution of the unexposed portion of the resist coating film is completed within 50 seconds).

Δ : The development property is good (dissolution of the unexposed portion of the resist coating film is completed after 50 seconds but within 100 seconds).

×: The development property is not good (complete dissolution of the unexposed portion

of the resist coating film takes 100 seconds or more).

[0121] "HEAT RESISTANCE"

With regard to the heat resistance evaluated on the basis of the change in the weight of a specimen between before and after a post-bake that was obtained by heating the specimen in a procedure of performing a pre-bake of $150^{\circ}\text{C} \times 30 \text{ min}$ and then the post-bake of $280^{\circ}\text{C} \times 60 \text{ min}$ in a thermogravimetry apparatus (Q50 made by TA Instruments), evaluation was performed as stated below, with Δ being a tolerance standard, from the viewpoint of industrial use.

○: The heat resistance is very good (a weight change less than or equal to 1.5%).

Δ : The heat resistance is good (a weight change beyond 1.5% and less than or equal to 2.0%).

×: The heat resistance is not good (a weight change beyond 2.0%).

[0122] <SYNTHESIS OF ACRYL COPOLYMER>

Synthesis Examples of the acryl copolymer in the invention are shown below. Incidentally, the invention is not limited only to the following methods. The production methods for acryl copolymers and characteristic values in Synthesis Examples are shown in Table 1. Furthermore, as for Synthesis Examples, the expression "part(s)" represents part(s) by weight.

[0123] The abbreviations of the (meth)acryl monomers and other monomers shown in Table 1 are as follows.

- Methyl methacrylate (MMA)
- Dodecyl methacrylate (DOMA)
- Stearyl methacrylate (SLMA)

Structures represented by the formula (D1) where n is 0:

- Methacrylic acid (MAA)
- Acrylic acid (AA)

Structures represented by the formula (E2):

- Styrene (St)
- 4-Methylstyrene (4MSt)

Structures represented by the formula (E1):

- Benzyl methacrylate (Bz-MA)

Structures represented by the formula (B):

- Methacrylic acid-2-dimethylaminoethyl (MLDA)
- Acrylic acid-2-dimethylaminoethyl (ALDA)

Structures represented by the formula (C):

- Methacrylic acid-2-dimethylaminoethyl hydrochloride (MLDA-Cl)

Structures represented by the formula (F):

- Acrylic acid-2-ethylhexyl (2EHA),
- Methacrylic acid-2-ethylhexyl (2EHMA)

Structures represented by the formula (D1):

- Acidic functional group-containing monomer mixture (made by Rhone-Poulenc, Inc.) (β -CEA)

Addition reaction monomer for introducing a structure (A) that has an ethylenic unsaturated group:

- Glycidyl methacrylate (GMA)

Polymerization initiating agent:

- Azobisisobutyronitrile (AIBN)
- Normal dodecyl mercaptan (MDM)

[0124] Adjustment of the base value shown in Table 1 was carried out by increasing and decreasing the charging amounts of the amino group-containing monomers (MLDA, ALDA and MLDA-Cl), and adjustment of the acid value was carried out by increasing and decreasing the charging amounts of the carboxyl group-containing monomer (AA, MAA and β -CEA).

[0125] Adjustment of the weight-average molecular weight shown in Table 1 was carried out by increasing and decreasing the charging amounts of the polymerization initiating agent (AIBN) and/or normal dodecyl mercaptan (MDM).

[0126] [Synthesis Example 1]

200 parts of a propylene glycol monoethyl ether acetate solvent was charged into a

pressure resistant vessel equipped with a stirring device, a thermometer, a reflux condenser and a dropping pump, and the reaction vessel was filled with nitrogen. Then, the temperature was raised to 90°C, and a mixture of 1 part of methacrylic acid-2-dimethylaminoethyl (MLDA), 32 parts of methyl methacrylate (MMA), 20 parts of methacrylic acid-2-ethylhexyl (2EHMA), 30 parts of styrene (St) and 17 parts of methacrylic acid (MAA) with 2.0 parts of azobisisobutyronitrile (AIBN) and 3.0 parts of normal dodecyl mercaptan (MDM) as polymerization initiating agents was dropped via the dropping pump over 3 hours to conduct copolymerization. After that, the gas in the reaction vessel was replaced with air, and 10 parts of glycidyl methacrylate (GMA) was dropped via the dropping pump over 1 hour to cause addition reaction, and the inside of the vessel was stirred for two more hours. As a result, an acryl copolymer (P-1) whose characteristic values were a base value of 5 mmol/100 g, an acid value of 75 mgKOH/g and a weight-average molecular weight of 7000 was obtained.

[0127] [Synthesis Example 2]

An acryl copolymer was manufactured in substantially the same manner as in Synthesis Example 1, except that the charging amounts of MMA and MLDA were changed to 31 parts and 2 parts, respectively. As a result, an acryl copolymer (P-2) having characteristic values shown in Table 1 was obtained.

[0128] [Synthesis Example 3]

An acryl copolymer was manufactured in substantially the same manner as in Synthesis Example 1, except that the charging amounts of MMA and MLDA were changed to 30 parts and 3 parts, respectively. As a result, an acryl copolymer (P-3) having characteristic values shown in Table 1 was obtained.

[0129] [Synthesis Example 4]

An acryl copolymer was manufactured in substantially the same manner as in Synthesis Example 1, except that the charging amounts of MMA and MLDA were changed to 29 parts and 4 parts, respectively. As a result, an acryl copolymer (P-4) having characteristic values shown in Table 1 was obtained.

[0130] [Synthesis Example 5]

An acryl copolymer was manufactured in substantially the same manner as in Synthesis Example 1, except that the charging amounts of MMA and MLDA were changed to 26 parts and 7 parts, respectively. As a result, an acryl copolymer (P-5) having characteristic values shown in Table 1 was obtained.

[0131] [Synthesis Example 6]

An acryl copolymer was manufactured in substantially the same manner as in Synthesis Example 1, except that MLDA was not used and the charging amount of MMA was changed to 33 parts. As a result, an acryl copolymer (P-6) having characteristic values shown in Table 1 was obtained.

[0132] [Synthesis Example 7]

An acryl copolymer was manufactured in substantially the same manner as in Synthesis Example 1, except that the charging amounts of MMA and MLDA were changed to 17 parts and 16 parts, respectively. As a result, an acryl copolymer (P-7) having characteristic values shown in Table 1 was obtained.

[Synthesis Example 8]

An acryl copolymer was manufactured in substantially the same manner as in Synthesis Example 3, except that MLDA was changed to ALDA. As a result, an acryl copolymer (P-8) having characteristic values shown in Table 1 was obtained.

[0133] [Synthesis Example 9]

An acryl copolymer was manufactured in substantially the same manner as in Synthesis Example 3, except that MLDA was changed to MLDA-Cl. As a result, an acryl copolymer (P-9) having characteristic values shown in Table 1 was obtained.

[0134] [Synthesis Example 10]

An acryl copolymer was manufactured in substantially the same manner as in Synthesis Example 3, except that the charging amounts of MMA and MAA were changed to 37 parts and 10 parts, respectively. As a result, an acryl copolymer (P-10) having characteristic values shown in Table 1 was obtained.

[0135] [Synthesis Example 11]

An acryl copolymer was manufactured in substantially the same manner as in

Synthesis Example 3, except that the charging amounts of MMA and MAA were changed to 27 parts and 20 parts, respectively. As a result, an acryl copolymer (P-11) having characteristic values shown in Table 1 was obtained.

[0136] [Synthesis Example 12]

An acryl copolymer was manufactured in substantially the same manner as in Synthesis Example 3, except that the charging amounts of MMA and MAA were changed to 23 parts and 24 parts, respectively. As a result, an acryl copolymer (P-12) having characteristic values shown in Table 1 was obtained.

[0137] [Synthesis Example 13]

An acryl copolymer was manufactured in substantially the same manner as in Synthesis Example 3, except that MAA was not used and the charging amount of MMA was changed to 47 parts. As a result, an acryl copolymer (P-13) having characteristic values shown in Table 1 was obtained.

[0138] [Synthesis Example 14]

An acryl copolymer was manufactured in substantially the same manner as in Synthesis Example 3, except that the charging amounts of MMA and MAA were changed to 40 parts and 7 parts. As a result, an acryl copolymer (P-14) having characteristic values shown in Table 1 was obtained.

[0139] [Synthesis Example 15]

An acryl copolymer was manufactured in substantially the same manner as in Synthesis Example 3, except that the charging amounts of MMA and MAA were changed to 15 parts and 32 parts, respectively. As a result, an acryl copolymer (P-15) having characteristic values shown in Table 1 was obtained.

[0140] [Synthesis Example 16]

An acryl copolymer was manufactured in substantially the same manner as in Synthesis Example 3, except that MAA was changed to AA. As a result, an acryl copolymer (P-16) having characteristic values shown in Table 1 was obtained.

[0141] [Synthesis Example 17]

An acryl copolymer was manufactured in substantially the same manner as in

Synthesis Example 3, except that the charging amount of MMA was changed to 14 parts, and 17 parts of MAA was changed to 33 parts of β -CEA. As a result, an acryl copolymer (P-17) having characteristic values shown in Table 1 was obtained.

[0142] [Synthesis Example 18]

An acryl copolymer was manufactured in substantially the same manner as in Synthesis Example 3, except that 2EHMA was changed to 2EHA. As a result, an acryl copolymer (P-18) having characteristic values shown in Table 1 was obtained.

[0143] [Synthesis Example 19]

An acryl copolymer was manufactured in substantially the same manner as in Synthesis Example 3, except that 2EHMA was changed to dodecyl methacrylate (DOMA). As a result, an acryl copolymer (P-19) having characteristic values shown in Table 1 was obtained.

[0144] [Synthesis Example 20]

An acryl copolymer was manufactured in substantially the same manner as in Synthesis Example 3, except that 2EHMA was changed to stearyl methacrylate (SLMA). As a result, an acryl copolymer (P-20) having characteristic values shown in Table 1 was obtained.

[0145] [Synthesis Example 21]

An acryl copolymer was manufactured in substantially the same manner as in Synthesis Example 3, except that 2EHMA was not used and the charging amount of MMA was changed to 50 parts. As a result, an acryl copolymer (P-21) having characteristic values shown in Table 1 was obtained.

[0146] [Synthesis Example 22]

An acryl copolymer was manufactured in substantially the same manner as in Synthesis Example 3, except that the charging amount of MDM was changed to 5.0 parts. As a result, an acryl copolymer (P-22) having characteristic values shown in Table 1 was obtained.

[0147] [Synthesis Example 23]

An acryl copolymer was manufactured in substantially the same manner as in

Synthesis Example 3, except that the charging amount of MDM was changed to 2.0 parts. As a result, an acryl copolymer (P-23) having characteristic values shown in Table 1 was obtained.

[0148] [Synthesis Example 24]

An acryl copolymer was manufactured in substantially the same manner as in Synthesis Example 3, except that the charging amount of MDM was changed to 1.0 part. As a result, an acryl copolymer (P-24) having characteristic values shown in Table 1 was obtained.

[0149] [Synthesis Example 25]

An acryl copolymer was manufactured in substantially the same manner as in Synthesis Example 3, except that MDM was not used. As a result, an acryl copolymer (P-25) having characteristic values shown in Table 1 was obtained.

[0150] [Synthesis Example 26]

An acryl copolymer was manufactured in substantially the same manner as in Synthesis Example 3, except that the charging amount of AIBN was changed to 6.0 parts. As a result, an acryl copolymer (P-26) having characteristic values shown in Table 1 was obtained.

[0151] [Synthesis Example 27]

An acryl copolymer was manufactured in substantially the same manner as in Synthesis Example 3, except that MDM was not used and the charging amount of AIBN was changed to 0.8 part. As a result, an acryl copolymer (P-27) having characteristic values shown in Table 1 was obtained.

[0152] [Synthesis Example 28]

An acryl copolymer was manufactured in substantially the same manner as in Synthesis Example 3, except that St was changed to 4MSt. As a result, an acryl copolymer (P-28) having characteristic values shown in Table 1 was obtained.

[0153] [Synthesis Example 29]

An acryl copolymer was manufactured in substantially the same manner as in Synthesis Example 3, except that St was changed to BzMA. As a result, an acryl

copolymer (P-29) having characteristic values shown in Table 1 was obtained.

[0154] [Synthesis Example 30]

An acryl copolymer was manufactured in substantially the same manner as in Synthesis Example 3, except that St was not used and the charging amount of MMA was changed to 60 parts. As a result, an acryl copolymer (P-30) having characteristic values shown in Table 1 was obtained.

[0155] [Table 1]

	Acryl copolymer	MMA (part(s))	St (part(s))	4M St (part(s))	Bz-MA (part(s))	MLDA (part(s))	ALDA (part(s))	MLDA-Cl (part(s))	MAA (part(s))	AA (part(s))	β -CEA (part(s))	2EHMA (part(s))	2EHA (part(s))	DOMA (part(s))	SI-MA (part(s))	GMA (part(s))	AIBN (part(s))	MDM (part(s))	Acid value (mgKOH/g)	Base value (mmol/100 g)	Weight-average molecular weight
Synthesis Example 1	P-1	32	30	-	-	1	-	-	17	-	-	20	-	-	-	10	2	3	75	5	7000
Synthesis Example 2	P-2	31	30	-	-	2	-	-	17	-	-	20	-	-	-	10	2	3	73	11	7000
Synthesis Example 3	P-3	30	30	-	-	3	-	-	17	-	-	20	-	-	-	10	2	3	71	18	7000
Synthesis Example 4	P-4	29	30	-	-	4	-	-	17	-	-	20	-	-	-	10	2	3	68	25	7000
Synthesis Example 5	P-5	26	30	-	-	7	-	-	17	-	-	20	-	-	-	10	2	3	67	42	7000
Synthesis Example 6	P-6	33	30	-	-	-	-	-	17	-	-	20	-	-	-	10	2	3	75	0	7000
Synthesis Example 7	P-7	17	30	-	-	16	-	-	17	-	-	20	-	-	-	10	2	3	65	95	7000
Synthesis Example 8	P-8	30	30	-	-	-	3	-	17	-	-	20	-	-	-	10	2	3	70	16	7000
Synthesis Example 9	P-9	30	30	-	-	-	-	3	17	-	-	20	-	-	-	10	2	3	71	15	7000
Synthesis Example 10	P-10	37	30	-	-	3	-	-	10	-	-	20	-	-	-	10	2	3	65	18	7000
Synthesis Example 11	P-11	27	30	-	-	3	-	-	20	-	-	20	-	-	-	10	2	3	90	18	7000
Synthesis Example 12	P-12	23	30	-	-	3	-	-	24	-	-	20	-	-	-	10	2	3	114	17	7000
Synthesis Example 13	P-13	47	30	-	-	3	-	-	-	-	-	20	-	-	-	10	2	3	0	20	7000
Synthesis Example 14	P-14	40	30	-	-	3	-	-	7	-	-	20	-	-	-	10	2	3	14	18	7000
Synthesis Example 15	P-15	15	30	-	-	3	-	-	32	-	-	20	-	-	-	10	2	3	157	17	7000
Synthesis Example 16	P-16	30	30	-	-	3	-	-	-	17	-	20	-	-	-	10	2	3	89	19	7000
Synthesis Example 17	P-17	14	30	-	-	3	-	-	-	-	33	20	-	-	-	10	2	3	30	18	7000
Synthesis Example 18	P-18	30	30	-	-	3	-	-	17	-	-	-	20	-	-	10	2	3	73	20	7000
Synthesis Example 19	P-19	30	30	-	-	3	-	-	17	-	-	-	-	20	-	10	2	3	70	20	7000
Synthesis Example 20	P-20	30	30	-	-	3	-	-	17	-	-	-	-	-	20	10	2	3	70	20	7000
Synthesis Example 21	P-21	50	30	-	-	3	-	-	17	-	-	-	-	-	-	10	2	3	71	20	7000
Synthesis Example 22	P-22	30	30	-	-	3	-	-	17	-	-	20	-	-	-	10	2	5	72	17	5000
Synthesis Example 23	P-23	30	30	-	-	3	-	-	17	-	-	20	-	-	-	10	2	2	73	18	11000
Synthesis Example 24	P-24	30	30	-	-	3	-	-	17	-	-	20	-	-	-	10	2	1	73	18	16000
Synthesis Example 25	P-25	30	30	-	-	3	-	-	17	-	-	20	-	-	-	10	2	0	73	17	20000
Synthesis Example 26	P-26	30	30	-	-	3	-	-	17	-	-	20	-	-	-	10	6	3	74	18	3000
Synthesis Example 27	P-27	30	30	-	-	3	-	-	17	-	-	20	-	-	-	10	0.8	0	74	18	39000
Synthesis Example 28	P-28	30	-	30	-	3	-	-	17	-	-	20	-	-	-	10	2	3	72	17	7000
Synthesis Example 29	P-29	30	-	-	30	3	-	-	17	-	-	20	-	-	-	10	2	3	73	18	7000
Synthesis Example 30	P-30	60	-	-	-	3	-	-	17	-	-	20	-	-	-	10	2	3	73	18	7000

[0156] <MAKING OF COLORING MATERIAL DISPERSION LIQUID AND PHOTSENSITIVE COLORING RESIN COMPOSITION>

[Example 1]

200 g of a nitride-of-titanium particle (Bk-1, made by Nisshin Engineering Inc.) produced by a thermal plasma method, 114 g of a 35-wt% propylene glycol monoethyl ether acetate solution of the acryl copolymer (P-1), 25 g of DISPERBYK LPN-21116 (DP-1, made by BYK Chemie, a 40-wt% propylene glycol monoethyl ether acetate solution) having a tertiary amino group and a quaternary ammonium salt as a high-molecular dispersing agent, and 661 g of propylene glycol monoethyl ether acetate (PMA) were charged into a tank, and was stirred by a homomixer (made by PRIMIX) for 20 minutes, whereby a preliminary dispersion liquid was obtained. After that, the preliminary dispersion liquid was supplied to an Ultra Apex Mill (made by KOTOBUKI INDUSTRIES) equipped with a centrifuge separation separator filled to 75 % with a 0.05-mm-φ zirconia bead (YTZ Ball, made by Neturen) , and dispersion was carried out at a rotation speed of 8 m/s for 3 hours, whereby a coloring material dispersion liquid 1 with the solid content concentration being 25 wt% and the coloring material /resin (weight ratio) = 80/20 was obtained. The obtained coloring material dispersion liquid 1 had a viscosity of 3.4 mPa·s immediately after being manufactured, and had a viscosity of 5.5 mPa·s one week after.

[0157] A photosensitive coloring resin composition made of a mixture of 33.00 g of this coloring material dispersion liquid 1 and 7.53 g of a 35-wt% propylene glycol monoethyl ether acetate solution of the acryl copolymer (P-1), 55.36 g of propylene glycol monoethyl ether acetate, 0.99 g of “ADEKA (registered trademark) OPTOMER” N-1919 (made by Asahi Denka Kogyo K.K.), 2.64 g of dipentaerythritol hexaacrylate (DHPA made by Nippon Kayaku Co., Ltd.), 0.45 g of 3-acryloxy propyl trimethoxysilane, and 0.04 g of BYK-333 (made by BYK Chemie GmbH) was prepared.

[0158] The obtained photosensitive coloring resin composition was coated on a nonalkali glass (“1737 material” made by Corning) substrate by a spin coater, and was pre-baked at 90°C for 10 minutes. After that, using an exposure machine “XG-5000”

made by DAINIPPON SCREEN CO. LTD., the pre-baked resin composition was exposed via a gray tone mask, and then a negative-type resist was developed by using a 0.045% potassium hydroxide aqueous solution. The development time was 33 seconds.

[0159] Furthermore, the dissolution time of the unexposed portion of the coating film developed was measured and evaluated by the test method described above. Results are shown in Table 2.

[0160] Incidentally, in Table 2, the kinds of the coloring material, the acryl copolymer, the high-molecular dispersing agent and the solvent constituting the coloring material dispersion liquid are indicated by abbreviations, and the compounding amounts (by weight) % of those components are indicated.

[0161] [Example 2 to Example 22 and Comparative Examples 1 to 8]

Table 2 shows details of results of evaluation of Examples 2 to 22 and Comparative Examples 1 to 8 in which coloring material dispersion liquids and photosensitive coloring resin compositions were produced substantially in the same manner as in Example 1, except that the acryl copolymers (P-2 to P-30) of which the characteristic value of the acid value, the base value, the weight-average molecular weight and a part of the unsaturated monomers was changed were used instead of the acryl copolymer (P-1).

[0162] Incidentally, with regard to the photosensitive coloring resin compositions obtained in Examples 3, 21 and 22 and Comparative Example 8, the heat resistances before and after the post-bake were evaluated by the method described above. Results thereof are shown in Table 2.

[0163] The dispersion stability of the coloring material dispersion liquid and the development property of the black matrix manufactured in each Example were both well achieved, and it can be understood that it is necessary to have an acryl copolymer of which the characteristic value of the base value, the acid value and the weight-average molecular weight are in specific ranges. Furthermore, it can be understood that it is necessary to introduce an aromatic ring into a side chain, in order to obtain sufficient heat resistance.

[0164] Furthermore, it can be understood that due to the introduction of a long-chain

acryl group into a side chain, the stability of the pigment dispersion liquid reached higher level.

[0165] [Table 2]

		Coloring material		Acryl copolymer		High-molecular dispersing agent		Solvent		Dispersion stability			Development property		Heat resistance	
		Kind	Amount added (wt%)	Kind	Amount added (wt%)	Kind	Amount added (wt%)	Kind	Amount added (wt%)	Assessment	Initial viscosity (mPa·s)	Time-dependent viscosity (mPa·s)	Assessment	Dissolution time (s)	Assessment	Weight change rate (%)
Example 1	Coloring material dispersion liquid 1	Bk-1	20	P-1	4	DP-1	1	PMA	75	Δ	3.4	5.5	○	25	-	-
Example 2	Coloring material dispersion liquid 2	Bk-1	20	P-2	4	DP-1	1	PMA	75	○	3.5	3.9	○	27	-	-
Example 3	Coloring material dispersion liquid 3	Bk-1	20	P-3	4	DP-1	1	PMA	75	○	4.2	4.6	○	33	○	1.1
Example 4	Coloring material dispersion liquid 4	Bk-1	20	P-4	4	DP-1	1	PMA	75	○	4.9	5.9	○	40	-	-
Example 5	Coloring material dispersion liquid 5	Bk-1	20	P-5	4	DP-1	1	PMA	75	Δ	5.5	9.1	Δ	64	-	-
Comparative Example 1	Coloring material dispersion liquid 6	Bk-1	20	P-6	4	DP-1	1	PMA	75	×	3.4	54.6	○	25	-	-
Comparative Example 2	Coloring material dispersion liquid 7	Bk-1	20	P-7	4	DP-1	1	PMA	75	×	12.5	88.5	Δ	94	-	-
Example 6	Coloring material dispersion liquid 8	Bk-1	20	P-8	4	DP-1	1	PMA	75	○	4.6	5.3	○	36	-	-
Example 7	Coloring material dispersion liquid 9	Bk-1	20	P-9	4	DP-1	1	PMA	75	○	4.5	4.8	Δ	52	-	-
Example 8	Coloring material dispersion liquid 10	Bk-1	20	P-10	4	DP-1	1	PMA	75	○	3.6	4.5	Δ	60	-	-
Example 9	Coloring material dispersion liquid 11	Bk-1	20	P-11	4	DP-1	1	PMA	75	○	5.2	7.0	○	26	-	-
Example 10	Coloring material dispersion liquid 12	Bk-1	20	P-12	4	DP-1	1	PMA	75	Δ	8.9	15.0	○	21	-	-
Comparative Example 3	Coloring material dispersion liquid 13	Bk-1	20	P-13	4	DP-1	1	PMA	75	○	3.1	3.4	×	>240	-	-
Comparative Example 4	Coloring material dispersion liquid 14	Bk-1	20	P-14	4	DP-1	1	PMA	75	○	3.6	4.0	×	118	-	-
Comparative Example 5	Coloring material dispersion liquid 15	Bk-1	20	P-15	4	DP-1	1	PMA	75	×	11.9	>100	○	16	-	-
Example 11	Coloring material dispersion liquid 16	Bk-1	20	P-16	4	DP-1	1	PMA	75	○	3.9	4.7	○	36	-	-
Example 12	Coloring material dispersion liquid 17	Bk-1	20	P-17	4	DP-1	1	PMA	75	○	5.8	7.0	○	44	-	-
Example 13	Coloring material dispersion liquid 18	Bk-1	20	P-18	4	DP-1	1	PMA	75	○	4.9	5.7	○	35	-	-
Example 14	Coloring material dispersion liquid 19	Bk-1	20	P-19	4	DP-1	1	PMA	75	○	5.5	6.5	○	40	-	-
Example 15	Coloring material dispersion liquid 20	Bk-1	20	P-20	4	DP-1	1	PMA	75	○	5.5	6.2	○	39	-	-
Example 16	Coloring material dispersion liquid 21	Bk-1	20	P-21	4	DP-1	1	PMA	75	Δ	3.6	6.2	○	34	-	-
Example 17	Coloring material dispersion liquid 22	Bk-1	20	P-22	4	DP-1	1	PMA	75	○	3.5	3.8	○	29	-	-

Table 2 (continued)

		Coloring material		Acryl copolymer		High-molecular dispersing agent		Solvent		Dispersion stability			Development property		Heat resistance	
		Kind	Amount added (wt%)	Kind	Amount added (wt%)	Kind	Amount added (wt%)	Kind	Amount added (wt%)	Assessment	Initial viscosity (mPa•s)	Time-dependent viscosity (mPa•s)	Assessment	Dissolution time (s)	Assessment	Weight change rate (%)
Example 18	Coloring material dispersion liquid 23	Bk-1	20	P-23	4	DP-1	1	PMA	75	○	5.7	7.2	○	44	-	-
Example 19	Coloring material dispersion liquid 24	Bk-1	20	P-24	4	DP-1	1	PMA	75	△	7.1	11.9	△	59	-	-
Example 20	Coloring material dispersion liquid 25	Bk-1	20	P-25	4	DP-1	1	PMA	75	△	12.8	20.8	△	80	-	-
Comparative Example 6	Coloring material dispersion liquid 26	Bk-1	20	P-26	4	DP-1	1	PMA	75	×	3.6	Unmeasurable	○	30	-	-
Comparative Example 7	Coloring material dispersion liquid 27	Bk-1	20	P-27	4	DP-1	1	PMA	75	×	16.9	>100	×	133	-	-
Example 21	Coloring material dispersion liquid 28	Bk-1	20	P-28	4	DP-1	1	PMA	75	○	4.9	5.8	○	38	○	1.3
Example 22	Coloring material dispersion liquid 29	Bk-1	20	P-29	4	DP-1	1	PMA	75	○	3.5	3.9	○	35	△	1.8
Comparative Example 8	Coloring material dispersion liquid 30	Bk-1	20	P-30	4	DP-1	1	PMA	75	○	3.3	3.6	○	33	×	4

[0166] [Example 23]

Table 3 shows results of evaluation of the development property of a photosensitive coloring resin composition and the dispersion stability of a coloring material dispersion liquid manufactured in substantially the same manner as in Example 3, except that 175 g of a nitride-of-titanium particle (Bk-1, made by Nisshin Engineering Inc.) produced by the thermal plasma method, 214 g of a 35-wt% propylene glycol monoethyl ether acetate solution of the acryl copolymer (P-3), and 611 g of propylene glycol monoethyl ether acetate (PMA) were used without adding a high-molecular dispersing agent.

[0167] Incidentally, in Table 3, the kinds of the coloring material, the acryl copolymer, the high-molecular dispersing agent and the solvent that constituted the coloring material dispersion liquids are indicated by abbreviations, and the compounded amounts (weights)% thereof are indicated.

[0168] [Comparative Example 9]

Table 3 shows results of evaluation of the development property of a photosensitive coloring resin composition and the dispersion stability of a coloring material dispersion liquid manufactured in substantially the same manner as in Example 23, except that the acryl copolymer (P-6) was used instead of the acryl copolymer (P-3).

[0169] [Example 24]

Table 3 shows results of evaluation of the development property of a photosensitive coloring resin composition and the dispersion stability of a coloring material dispersion liquid manufactured in substantially the same manner as in Example 3, except that DISPERBYK LPN-6919 (DP-2, made by BYK Chemie, a 40-wt% propylene glycol monoethyl ether acetate solution) having a tertiary amino group was used as a high-molecular dispersing agent, instead of DISPERBYK LPN-21116 (DP-1, made by BYK Chemie, a 40-wt% propylene glycol monoethyl ether acetate solution).

[0170] [Example 25]

Table 3 shows results of evaluation of the development property of a photosensitive coloring resin composition and the dispersion stability of a coloring material dispersion liquid manufactured in substantially the same manner as in Example 3, except that

DISPERBYK-2001 (DP-3, made by BYK Chemie a 40-wt% propylene glycol monoethyl ether acetate solution) having a carboxyl group and a quaternary ammonium salt was used as a high-molecular dispersing agent, instead of DISPERBYK LPN-21116 (DP-1, made by BYK Chemie, a 40-wt% propylene glycol monoethyl ether acetate solution).

[0171] From results of Examples 23 to 25 and Comparative Example 9, it can be understood that due to the use of the acryl copolymer of the invention, dispersion stabilization becomes possible without adding a high-molecular dispersing agent; however, it can be understood that in order to further stabilize the dispersion, it is preferable to add a high-molecular dispersing agent and, in particular, it is more preferable to use a high-molecular dispersing agent having a tertiary amino group.

[0172] [Example 26]

Table 3 shows results of evaluation of the development property of a photosensitive coloring resin composition and the dispersion stability of a coloring material dispersion liquid manufactured in substantially the same manner as in Example 3, except that 220 g of a nitride-of-titanium particle (Bk-1, made by Nisshin Engineering Inc.) produced by the thermal plasma method, 57 g of a 35-wt% propylene glycol monoethyl ether acetate solution of the acryl copolymer (P-3), 25 g of DISPERBYK LPN-21116 (DP-1, made by BYK Chemie, a 40-wt% propylene glycol monoethyl ether acetate solution) as a high-molecular dispersing agent, and 698 g of propylene glycol monoethyl ether acetate (PMA) were used.

[0173] [Example 27]

Table 3 shows results of evaluation of the development property of a photosensitive coloring resin composition and the dispersion stability of a coloring material dispersion liquid manufacture in substantially the same manner as in Example 3, except that 175 g of a nitride-of-titanium particle (Bk-1, made by Nisshin Engineering Inc.) produced by the thermal plasma method, 186 g of a 35-wt% propylene glycol monoethyl ether acetate solution of the acryl copolymer (P-3), 25 g of DISPERBYK LPN-21116 (DP-1 made by BYK Chemie, a 40-wt% propylene glycol monoethyl ether acetate solution) as a high-molecular dispersing agent, and 614 g of propylene glycol monoethyl ether acetate

(PMA) were used.

[0174] From results of Example 3 and Examples 26 to 27, it can be understood that it is more preferable that the acryl copolymer of the invention be used and that, as for the coloring material component /resin component weight composition ratio, the resin component be greater in amount than 90/10.

[0175] [Example 28]

175 g of a high-resistance carbon black (Bk-2, made by Cabot Corr.), 171 g of a 35-wt% propylene glycol monoethyl ether acetate solution of the acryl copolymer (P-3), 38 g of DISPERBYK LPN-21116 (DP-1, made by BYK Chemie, a 40-wt% propylene glycol monoethyl ether acetate solution) as a high-molecular dispersing agent, and 616 g of propylene glycol monoethyl ether acetate (PMA) were charged into a tank, and stirred for 20 minutes by a homomixer (made by PRIMIX) to obtain a preliminary dispersion liquid. After that, the preliminary dispersion liquid was supplied into an Ultra Apex Mill (made by KOTOBUKI INDUSTRIES) equipped with a centrifugal separation separator filled to 75% with a 0.05-mm-φ zirconia bead (made by Neturen, YTZ Ball), and was dispersed at a rotation speed of 8 m/s for 3 hours to obtain a coloring material dispersion liquid 37 with the solid content concentration being 25 wt% and the coloring material /resin (weight ratio) = 70/30.

[0176] 37.71 g of this coloring material dispersion liquid 37, 4.48 g of a 35-wt% propylene glycol monoethyl ether acetate solution of the acryl copolymer (P-1), 53.80 g of propylene glycol monoethyl ether acetate, 0.96 g of “ADEKA (registered trademark) OPTOMER” N-1919 (made by Asahi Denka Kogyo K.K.), 2.55 g of dipentaerythritol hexaacrylate (DHPA made by Nippon Kayaku Co., Ltd.), 0.45 g of 3-acryloxy propyl trimethoxysilane, and 0.04 g of BYK-333 (made by BYK Chemie GmbH) were mixed to manufacture a photosensitive coloring resin composition, which was then subjected to development property evaluation in substantially the same manner as in Example 1. Results of evaluation of the development property of the photosensitivity resin composition and the dispersion stability of the coloring material dispersion liquid are shown in Table 3.

[0177] [Comparative Example 10]

Table 3 shows the development property of a photosensitivity resin composition and the dispersion stability of a coloring material dispersion liquid manufactured in substantially the same manner as in Example 28, except that as the acryl copolymer, P-6 was used instead of P-3.

[0178] [Example 29]

120 g of an organic pigment PR 177 (R-1, made by Dainichiseika K.K.), 114 g of a 35-wt% propylene glycol monoethyl ether acetate solution of the acryl copolymer (P-3), 100 g of DISPERBYK LPN-21116 (DP-1, made by BYK Chemie, a 40-wt% propylene glycol monoethyl ether acetate solution) as a high-molecular dispersing agent, and 666 g of propylene glycol monoethyl ether acetate (PMA) were charged into a tank, and stirred for 20 minutes by a homomixer (made by PRIMIX) to obtain a preliminary dispersion liquid. After that, the preliminary dispersion liquid was supplied into an Ultra Apex Mill (made by KOTOBUKI INDUSTRIES) equipped with a centrifugal separation separator filled to 75% with 0.05-mm-φ zirconia bead (made by Neturen, YTZ Ball), and was dispersed at a rotation speed of 8 m/s for 3 hours to obtain a coloring material dispersion liquid 39 with the solid content concentration being 20 wt% and the coloring material /resin (weight ratio) = 60/40. The dispersion stability of the coloring material dispersion liquid obtained was evaluated in substantially the same manner as in Example 1.

[0179] 37.50 g of this coloring material dispersion liquid 39, 7.29 g of a 35-wt% of a propylene glycol monoethyl ether acetate solution of the acryl copolymer (P-1), 50.26 g of propylene glycol monoethyl ether acetate, 0.41 g of “ADEKA (registered trademark) OPTOMER” N-1919 (made by Asahi Denka Kogyo K.K.), 4.05 g of dipentaerythritol hexaacrylate (DHPA made by Nippon Kayaku Co., Ltd.), 0.45 g of 3-acryloxy propyl trimethoxysilane, and 0.04 g of BYK-333 (made by BYK Chemie GmbH) were mixed to manufacture a photosensitive coloring resin composition, which was then subjected to development property evaluation in substantially the same manner as in Example 1.

[0180] [Comparative Example 11]

Table 3 shows results of evaluation of the development property of a photosensitivity resin composition and the dispersion stability of a coloring material dispersion liquid manufactured in substantially the same manner as in Example 29, except that as the acryl copolymer, P-6 was used instead of P-3.

[0181] [Example 30]

50 g of a dye AR289 (R-2, made by Chugai Kasei Company, Limited), 357 g of a 35-wt% propylene glycol monoethyl ether acetate solution of the acryl copolymer (P-3), 63 g of DISPERBYK LPN-21116 (DP-1, made by BYK Chemie, a 40-wt% propylene glycol monoethyl ether acetate solution) as a high-molecular dispersing agent, and 530 g of propylene glycol monoethyl ether acetate (PMA) were charged into a tank, and stirred for 20 minutes by a homomixer (made by PRIMIX) to obtain a preliminary dispersion liquid. After that, the preliminary dispersion liquid was supplied into an Ultra Apex Mill (made by KOTOBUKI INDUSTRIES) equipped with a centrifugal separation separator filled to 75% with a 0.05-mm- ϕ zirconia bead (YTZ Ball, made by Neturen), and was dispersed at a rotation speed of 8 m/s for 3 hours to obtain a coloring material dispersion liquid 41 with the solid content concentration being 20 wt% and the coloring material /resin (weight ratio) = 25/75. The dispersion stability of the coloring material dispersion liquid obtained was evaluated in substantially the same manner as in Example 1.

[0182] 45.00 g of this coloring material dispersion liquid 41, 1.03 g of a 35-wt% propylene glycol monoethyl ether acetate solution of the acryl copolymer (P-1), 48.33 g of propylene glycol monoethyl ether acetate, 0.29 g of "ADEKA (registered trademark) OPTOMER" N-1919 (made by Asahi Denka Kogyo K.K.), 4.86 g of dipentaerythritol hexaacrylate (DHPA made by Nippon Kayaku Co., Ltd.), 0.45 g of 3-acryloxy propyl trimethoxysilane, and 0.04 g of BYK-333 (made by BYK Chemie GmbH) were mixed to manufacture a photosensitive coloring resin composition, which was then subjected to development property evaluation in substantially the same manner as in Example 1.

[0183] [Comparative Example 12]

Table 3 shows results of evaluation of the development property of a

photosensitivity resin composition and the dispersion stability of a coloring material dispersion liquid manufactured in substantially the same manner as in Example 30, except that as the acryl copolymer, P-6 was used instead of P-3.

[0184] [Example 31]

160 g of an Ag nanoparticle (Ag-1, made by Daiwa Kasei K.K.), 57 g of a 35-wt% propylene glycol monoethyl ether acetate solution of the acryl copolymer (P-3), 50 g of DISPERBYK LPN-21116 (DP-1, made by BYK Chemie, a 40-wt% propylene glycol monoethyl ether acetate solution) as a high-molecular dispersing agent, and 733 g of propylene glycol monoethyl ether acetate (PMA) were charged into a tank, and was stirred for 20 minutes by a homomixer (made by PRIMIX) to obtain a preliminary dispersion liquid. After that, the preliminary dispersion liquid was supplied into an Ultra Apex Mill (made by KOTOBUKI INDUSTRIES) equipped with a centrifugal separation separator filled to 75% with a 0.05-mm-φ zirconia bead (YTZ Ball, made by Neturen), and was dispersed at a rotation speed of 8 m/s for 3 hours to obtain a coloring material dispersion liquid 43 with the solid content concentration being 20 wt% and the coloring material /resin (weight ratio)) = 80/20. The dispersion stability of the coloring material dispersion liquid obtained was evaluated in substantially the same manner as in Example 1.

[0185] 46.88 g of this coloring material dispersion liquid 43, 6.37 g of a 35-wt% propylene glycol monoethyl ether acetate solution of the acryl copolymer (P-1), 43.36 g of propylene glycol monoethyl ether acetate, 0.79 g of “ADEKA (registered trademark) OPTOMER” N-1919 (made by Asahi Denka Kogyo K.K.), 2.11 g of dipentaerythritol hexaacrylate (DHPA made by Nippon Kayaku Co., Ltd.), 0.45 g of 3-acryloxy propyl trimethoxysilane, and 0.04 g of BYK-333 (made by BYK Chemie GmbH) were mixed to manufacture a photosensitive coloring resin composition, which was then subjected to development property evaluation in substantially the same manner as in Example 1.

[0186] [Comparative Example 13]

Table 3 shows results of evaluation of the development property of a photosensitivity resin composition and the dispersion stability of a coloring material

dispersion liquid manufactured in substantially the same manner as in Example 31, except that as the acryl copolymer, P-6 was used instead of P-3.

[0187] From results of Examples 28 to 31 and Comparative Examples 10 to 13, it can be understood that, by using the acryl copolymer of the invention, the dispersion stabilization can be accomplished with regard to not only inorganic pigments but also organic pigments, dyes and metal fine particles.

[0188][Table 3]

		Coloring material		Acryl copolymer		High-molecular dispersing agent		Solvent		Dispersion stability			Development property	
		Kind	Amount added (wt%)	Kind	Amount added (wt%)	Kind	Amount added (wt%)	Kind	Amount added (wt%)	Assessment	Initial viscosity (mPa•s)	Time-dependent viscosity (mPa•s)	Assessment	Dissolution time (s)
Example 23	Coloring material dispersion liquid 31	Bk-1	17.5	P-3	7.5	-	-	PMA	75	Δ	4.5	8.3	○	25
Comparative Example 9	Coloring material dispersion liquid 32	Bk-1	17.5	P-6	7.5	-	-	PMA	75	×	4.7	>100	○	23
Example 24	Coloring material dispersion liquid 33	Bk-1	20	P-3	4	DP-2	1	PMA	75	○	4.3	4.9	○	44
Example 25	Coloring material dispersion liquid 34	Bk-1	20	P-3	4	DP-3	1	PMA	75	Δ	4.1	6.4	○	27
Example 26	Coloring material dispersion liquid 35	Bk-1	22	P-3	2	DP-1	1	PMA	75	Δ	5.0	9.7	○	29
Example 27	Coloring material dispersion liquid 36	Bk-1	17.5	P-3	6.5	DP-1	1	PMA	75	○	3.8	3.9	○	35
Example 28	Coloring material dispersion liquid 37	Bk-2	17.5	P-3	6	DP-1	1.5	PMA	75	○	3.8	4.1	○	29
Comparative Example 10	Coloring material dispersion liquid 38	Bk-2	17.5	P-6	6	DP-1	1.5	PMA	75	×	4.6	11.3	○	24
Example 29	Coloring material dispersion liquid 39	R-1	12	P-3	4	DP-1	4	PMA	80	○	4.8	5.5	○	41
Comparative Example 11	Coloring material dispersion liquid 40	R-1	12	P-6	4	DP-1	4	PMA	80	×	5.3	12.1	○	37
Example 30	Coloring material dispersion liquid 41	R-2	5	P-3	12.5	DP-1	2.5	PMA	80	○	4.5	4.9	○	36
Comparative Example 12	Coloring material dispersion liquid 42	R-2	5	P-6	12.5	DP-1	2.5	PMA	80	×	6.5	15.2	○	31
Example 31	Coloring material dispersion liquid 43	Ag-1	16	P-3	2	DP-1	2	PMA	80	○	4.5	4.8	○	30
Comparative Example 13	Coloring material dispersion liquid 44	Ag-1	16	P-6	2	DP-1	2	PMA	80	×	7.3	23.0	○	27

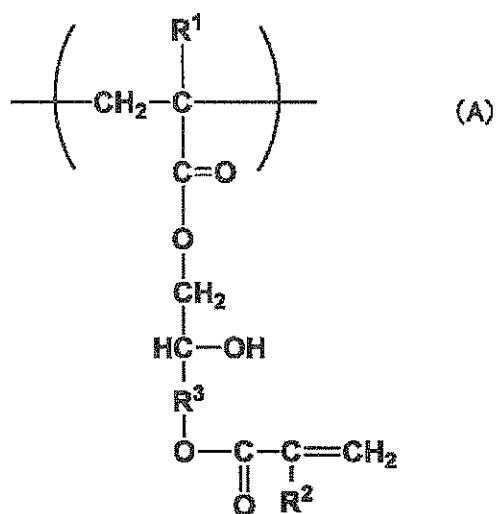
Industrial applicability

[0189] The coloring material dispersion liquid of the invention is excellent in dispersion stability and is good in time-dependent viscosity stability, even when having a composition that contains the coloring material at a high concentration. Furthermore, by preparing a photosensitive coloring resin composition by using the coloring material dispersion liquid of the invention, it becomes possible to form a coating film excellent in alkaline development solubility and heat resistance. Therefore, it becomes possible to form high-performance colored patterns of color filter substrates for liquid crystal display apparatuses, sensor substrates for touch panels, etc., at good production efficiency.

Claims

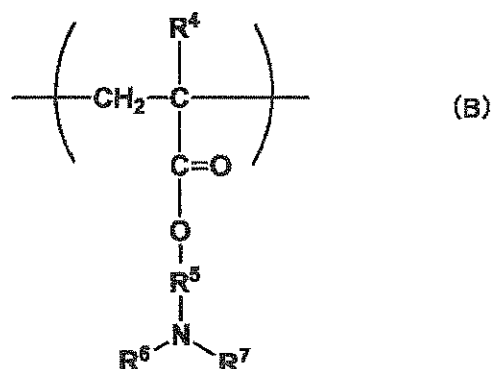
[Claim 1] A coloring material dispersion liquid containing at least a coloring material, an acryl copolymer and an organic solvent, the coloring material dispersion liquid being characterized in that the acryl copolymer has at least a structure represented by a formula (A) below which has in a side chain an ethylenic unsaturated group, a structure represented by a formula (B) below which has in a side chain a tertiary amino group and/or a structure represented by a formula (C) below which has in a side chain a quaternary ammonium salt, a structure (D) having in a side chain a carboxyl group, and a structure (E) having an aromatic ring, and that, as for the acryl copolymer, a base value is 5 to 70 mmol/100 g, an acid value is 50 to 120 mgKOH/g, and a weight-average molecular weight in terms of polystyrene by gel permeation chromatography is 5,000 to 30,000.

[Chem. 1]



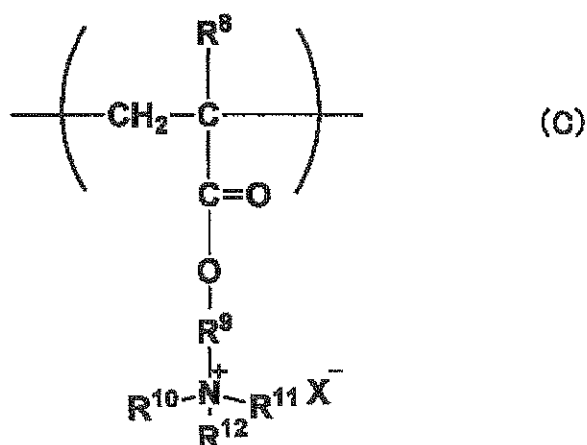
(In the formula, R^1 and R^2 , independently of each other, represent a hydrogen atom or a methyl group, and R^3 represents a species selected from alkylene groups whose carbon number is 1 to 4, divalent alicyclic hydrocarbon groups whose carbon number is 3 to 6 and divalent aromatic hydrocarbon groups whose carbon number is 6 to 10.)

[Chem. 2]



(In the formula, R^4 represents a hydrogen atom or a methyl group, R^5 represents a species selected from alkylene groups whose carbon number is 1 to 4, divalent alkoxy groups whose carbon number is 1 to 4, divalent alicyclic hydrocarbon groups whose carbon number is 3 to 6 and divalent aromatic hydrocarbon groups whose carbon number is 6 to 10, and R^6 and R^7 , independently of each other, represent a species selected from alkyl groups whose carbon number is 1 to 4, alkoxy groups whose carbon number is 1 to 4, alicyclic hydrocarbon groups whose carbon number is 3 to 6 and aromatic hydrocarbon groups whose carbon number is 6 to 10.)

[Chem. 3]

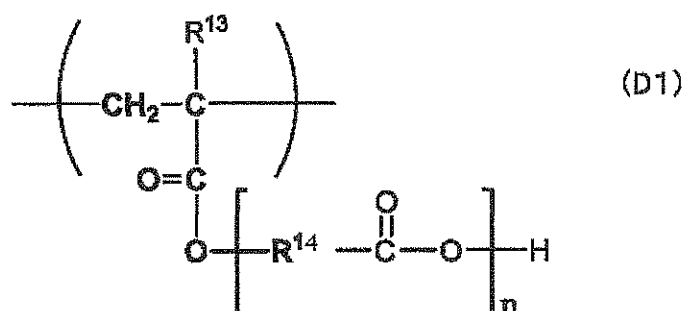


(In the formula, R^8 represents a hydrogen atom or a methyl group, R^9 represents a species selected from alkylene groups whose carbon number is 1 to 4, divalent alkoxy groups

whose carbon number is 1 to 4, divalent alicyclic hydrocarbon groups whose carbon number is 3 to 6 and divalent aromatic hydrocarbon groups whose carbon number is 6 to 10, R^{10} , R^{11} and R^{12} , independently of each other, represent a species selected from alkyl groups whose carbon number is 1 to 4, alkoxy groups whose carbon number is 1 to 4, alicyclic hydrocarbon groups whose carbon number is 3 to 6 and aromatic hydrocarbon groups whose carbon number is 6 to 10, and X represents any one of bromine, chlorine, iodine, hydrogen sulfate and hydroxide.)

[Claim 2] The coloring material dispersion liquid according to claim 1, wherein the structure (D) having the carboxyl group is represented by a formula (D1) below.

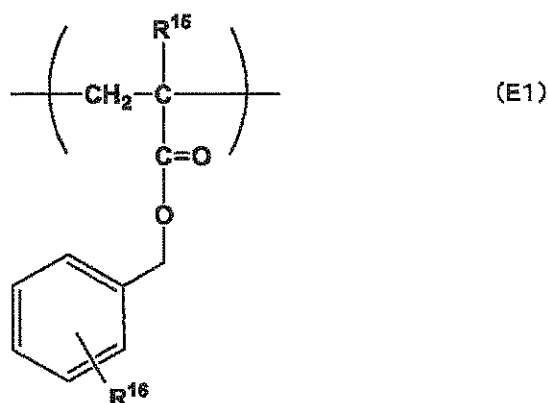
[Chem. 4]



(In the formula, R^{13} represents a hydrogen atom or a methyl group, R^{14} represents a species selected from alkylene groups whose carbon number is 1 to 4, divalent alicyclic hydrocarbon chains whose carbon number is 3 to 6 and divalent aromatic hydrocarbon chains whose carbon number is 6 to 10, and n represents an integer of 0 to 6, and n may be a single n or a mixture of a plurality of n's.)

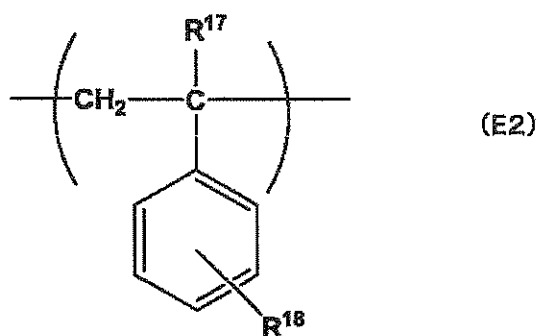
[Claim 3] The coloring material dispersion liquid according to claim 1 or 2, wherein the structure (E) having the aromatic ring is represented by a formula (E1) or (E2) below.

[Chem. 5]



(In the formula, R^{15} represents a hydrogen atom or a methyl group, and R^{16} represents a species selected from hydrogen, alkyl groups whose carbon number is 1 to 4, alkoxy groups whose carbon number is 1 to 4, alicyclic hydrocarbon groups whose carbon number is 3 to 6, aromatic hydrocarbon groups whose carbon number is 6 to 10, halogen atoms, ester groups, acyl groups and a nitro group.)

[Chem. 6]

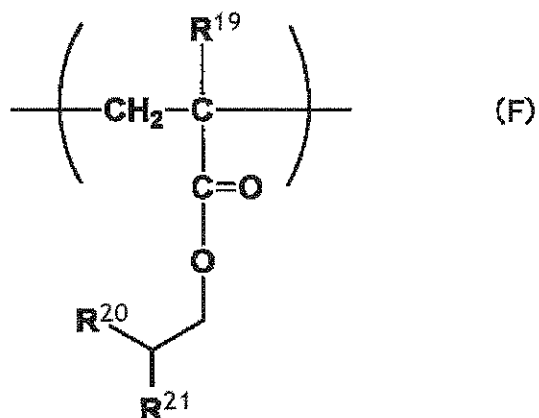


(In the formula, R^{17} represents a hydrogen atom or a methyl group, and R^{18} represents a species selected from hydrogen, alkyl groups whose carbon number is 1 to 4, alkoxy groups whose carbon number is 1 to 4, alicyclic hydrocarbon groups whose carbon number is 3 to 6, aromatic hydrocarbon groups whose carbon number is 6 to 10, halogen atoms, ester groups, acyl groups and a nitro group.)

[Claim 4] The coloring material dispersion liquid according to claim 1, 2 or 3, wherein the acryl copolymer further has a structure represented by a formula (F) below which has

in a side chain a carboxylic acid ester.

[Chem. 7]



(In the formula, R^{19} represents a hydrogen atom or a methyl group, R^{20} represents a hydrogen atom or an alkyl group whose carbon atom number 1 to 20, and R^{21} represents an alkyl group whose carbon atom number 2 to 40.)

[Claim 5] The coloring material dispersion liquid according to claim 4, wherein a total carbon number of the R^{20} and the R^{21} is greater than or equal to 4.

[Claim 6] The coloring material dispersion liquid according to any one of claims 3 to 5, having a structure represented by a formula (E2).

[Claim 7] The coloring material dispersion liquid according to any one of claims 1 to 6, containing, in addition to the acryl copolymer, a high-molecular dispersing agent that has at least a tertiary amino group.

[Claim 8] A photosensitive coloring resin composition containing at least the coloring material dispersion liquid according to any one of claims 1 to 7, a multifunctional acryl monomer and a photo-radical polymerization initiating agent.