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(54) LIQUID DEVELOPING AGENT AND PROCESS FOR PRODUCING THE SAME

(57) This invention provides a liquid developing agent for electrophotography or electrostatic recording that can realize a high solid content and has excellent developing properties. The liquid developing agent is **characterized in that** colored chips produced by heat kneading a pigment with a thermoplastic resin are dispersed by wet pulverization in an electrically insulating hydrocarbon solvent containing at least one pigment dispersant selected from the group consisting of specific modified novolak resins (A) having an aromatic ring and a ring opened structure of an epoxy group by a hydroxycarboxylic acid-derived carboxyl group, and copolymers (B).

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Description

TECHNICAL FIELD

[0001] The present invention relates to a liquid developing agent for electrophotography and electrostatic recording used in a printing machine, copier, printer, and facsimile.

BACKGROUND ART

[0002] Liquid developing agents for electrophotography and electrostatic recording used in a copier, printer, and facsimile are broadly classified into a dry developing agent and a liquid developing agent; and it is thought that particle diameter of toner particle is smaller in a liquid developing agent, which is greatly advantageous to obtain a high quality photographic image. From this reason, in market there have been required liquid developing agents capable of forming a high quality photographic image with high image density and low fogging.

[0003] As liquid developing agents, generally, toner particles that colorants such as pigment covered with thermoplastic resins are dispersed in an electrically insulating solvent have been used.

[0004] As one of relatively easy production methods for obtaining the liquid developing agent, there is proposed a process for producing a liquid developing agent by a wet pulverization method that a colorant and a resin are kneaded by a kneading machine such as a kneader and three-roll mill while heating at a temperature of at least a melting point of the resin, after cooling, the resultant mixture is subjected to dry pulverization, the pulverized powder is subjected to wet pulverization using a dispersant and electrically insulating nonaqueous solvent to give a concentrated solution of toner, further, dispersed in an electrically insulating nonaqueous solvent containing a charge controlling agent to produce a liquid developing agent (see, e.g., Japanese Unexamined Patent Publication No. 60-021056A and Japanese Unexamined Patent Publication No. 05-134468A.

[0005] In recent years, however, from the points of higher developing speed, mileage and recovery of electrically insulating solvents, requirements on further high solid content of liquid developing agent have been done, but in the above-described method, it is fundamentally difficult to maintain dispersion stability and charging characteristics sufficiently, thus there has had a problem that increase in viscosity and lowering of electric resistance occur with increase in the solid content concentration of a liquid developing agent.

DISCLOSURE OF INVENTION

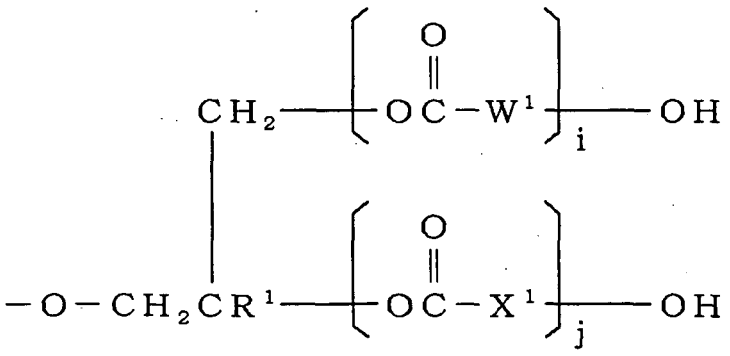
[0006] In this situation, it is an object of the present invention to provide a liquid developing agent that can realize a high solid content and has excellent developing properties, and a process for producing the same.

[0007] The present inventors have keenly studied to solve the above-described problems, as a result, have found the knowledge that can solve all the problems and completed the present invention as follows: a pigment and thermoplastic resin are heat kneaded, then further, which is subjected to wet pulverization in an electrically insulating hydrocarbon solvent containing a specific pigment dispersant having an aromatic ring and a ring-opened structure of an epoxy group by a hydroxycarboxylic acid-derived carboxyl group to produce a liquid developing agent.

[0008] Namely, the present invention provides the following liquid developing agent and a process for producing the same.

[1] A liquid developing agent where a colored chip obtained by heat kneading a pigment with a thermoplastic resin is dispersed by wet pulverization in an electrically insulating hydrocarbon solvent dispersing at least one pigment dispersant selected from the group consisting of the following modified novolak resin (A) and a copolymer (B) having an aromatic ring and a ring-opened structure of an epoxy group by a hydroxycarboxylic acid-derived carboxyl group:

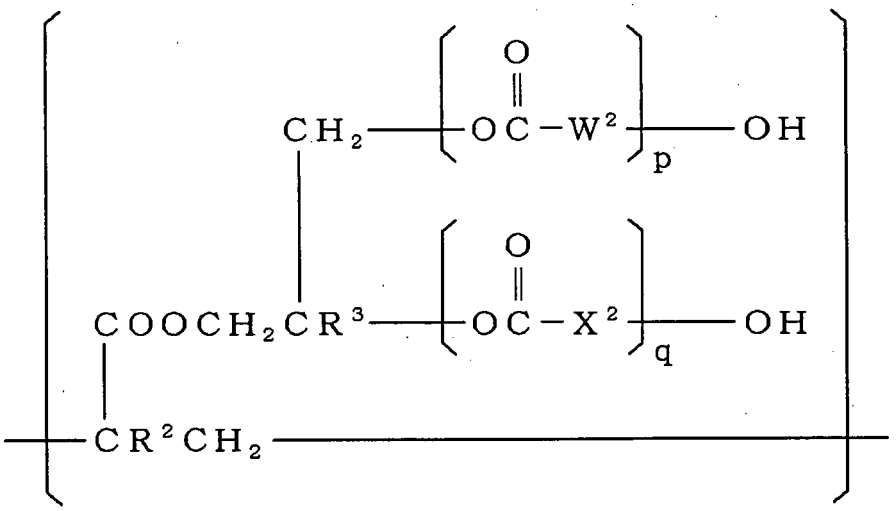
Modified novolak resin (A): a modified novolak resin having a novolak resin-derived aromatic ring and at least one group shown by a general formula (1) by ring-opening of an epoxy group by a hydroxycarboxylic acid-derived carboxyl group:



(1)

wherein an oxygen atom at the far left is derived from an oxygen atom contained in an aromatic hydroxyl group of a novolak resin, W^1 and X^1 each independently represent a divalent hydrocarbon group with carbon numbers of 1 to 19, i and j each independently represent an integer of i = 1 to 30 and j = 0 to 30, and R^1 represents a hydrogen atom or a methyl group.

Copolymer (B): a copolymer with a weight-average molecular weight of 3000 to 100000, having, in said copolymer, the amount corresponding to at least 10 mol% of the recurring unit shown by a general formula (2), and the amount corresponding to at least 10 mol% of at least one kind selected from the recurring units shown by a general formula (3) and a general formula (4)



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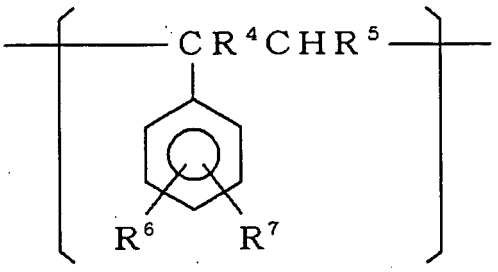

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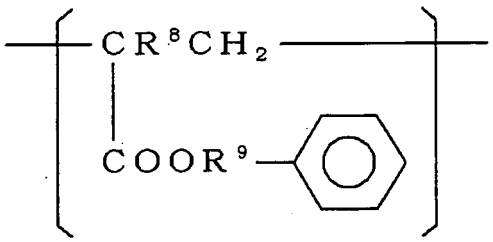


(4)

wherein W^2 and X^2 each independently represent a divalent hydrocarbon group with carbon numbers of 1 to 19, p and q each independently represent an integer of p = 1 to 30, and q = 0 to 30, R^2, R^3 and R^4 each independently represent a hydrogen atom or a methyl group, R^5 represents a hydrogen atom or a halogen atom, R^6 and R^7 each independently represent a hydrogen atom, a hydrocarbon group with carbon numbers of 1 to 5, an alkoxy group with carbon numbers of 1 to 5, an aryloxy group with carbon numbers of 6 to 10, or a halogen atom, R^8 represents a hydrogen atom or a methyl group, and R^9 represents a direct bond or a methylene group.

[2] The liquid developing agent described in the [1], wherein the concentration of the total solid content in a liquid developing agent was 13 to 50 % by mass.

[3] The liquid developing agent described in the [1] or [2], wherein the composition of the pigment dispersant is 2 to 100 parts by mass relative to 100 parts by mass of the colored chip.

[4] The liquid developing agent described in any one of the [1] to [3], wherein said electrically insulating hydrocarbon solvent is a high boiling point paraffin solvent.

[5] A process for producing the liquid developing agent described in any one of the [1] to [4], wherein the colored chip obtained by heat kneading a pigment with a thermoplastic resin is subjected to dry pulverization into a coarse pulverized powder beforehand, further, said pulverized powder is subjected to wet pulverization in an electrically insulating hydrocarbon solvent dissolving at least one pigment dispersant selected from the group consisting of said modified novolak resin (A) and said copolymer (B).

BEST MODE FOR CARRYING OUT THE INVENTION

[0009] The present invention will be described in detail below.

[0010] First, constituent materials used in the liquid developing agent of the present invention are explained.

[0011] As the pigment used in the present invention, inorganic pigments and organic pigments conventionally used in a liquid developing agent can be used without limitation in particular, for example, there are listed inorganic pigments such as carbon black including acetylene black; graphite, colcothar, chrome yellow and ultramarine blue; and organic pigments such as azo pigments, condensed azo pigments, lake pigments, phthalocyanine pigments, isoindoline pigments, anthraquinone pigments and quinacridone pigments. Regarding various kinds of hues of organic pigments, as magenta-type organic pigments, there are listed qunacridone pigments such as qunacridone red; azo pigments such as permanent red; condensed azo pigments such as condensed azo red, and perylene pigments such as perylene red. As cyanogen-type pigments, phtahlocyanine pigments such as metal-free phthalocyanine blue, phthalocyanine blue and fast sky blue are listed. As yellow-type organic pigments, there are listed monoazo pigments such as hansa yellow, disazo pigments such as benzine yellow and permanent yellow; and condensed azo pigments such as condensed azo yellow. As green-type pigments, phthalocyanine pigments such as phthalocyanine green are listed. These pigments can be used alone or in mixture of at least 2 kinds thereof.

[0012] The content of pigment in a liquid developing agent is not particularly limited, it is preferably 1 to 20 parts by mass in the 100 parts by mass of final liquid developing agent from the point of image density.

[0013] As a thermoplastic resin used in the present invention, known thermoplastic resins used in a liquid developing agent can be adopted, which are insoluble in an electrically insulating hydrocarbon solvent, preferably have a low degree of swelling to electrically insulating hydrocarbon solvents. When the degree of swelling of thermoplastic resin is high, it is difficult to realize a high solid content, which tends to pose a problem that flogging and stain in non-image part of photographic image take place when developing speed is increased.

[0014] The thermoplastic resins include, for example, synthetic resins or natural resins such as a polyester resin, epoxy resin, acryl resin, styrene resin, styrene-acryl copolymer resin, polyvinylchloride resin, polyvinyl acetate resin, polyethylene resin, polypropylene resin, polyurethane resin, polyvinyl butyral resin, rosin resin, modified rosin resin,

terpene resin, phenol resin, aliphatic hydrocarbon resin and aromatic petroleum resin. These thermoplastic resins can be used alone or in mixture of at least 2 kinds thereof.

[0015] Additionally the ratio of the sum of pigment and thermoplastic resin in the liquid developing agent of the present invention is preferably 10 to 50 % by mass, more preferably 15 to 40 % by mass. When the ratio of the sum of pigment and thermoplastic resin is less than the above-described range, there is an instance that a sufficient concentration is not obtained as a liquid developing agent, when more than the above-described range, there is an instance that a problem of excess increase in viscosity of liquid developing agent is posed.

[0016] As the electrically insulating hydrocarbon solvent used in the present invention, it is a solvent which does not solve the above-described thermoplastic resin, there can be used one with a volume resistivity (about 10^{11} to 10^{16} Ω·cm) not disturbing electrostatic latent image, such as an aliphatic hydrocarbon, an alicyclic hydrocarbon, an aromatic hydrocarbon and a halogenated hydrocarbon. Among them, from the viewpoints of odor, non-toxicity and cost, preferable are paraffin solvents with a high boiling point (boiling point of at least 150°C under normal pressure) such as n-paraffin solvents, isoparaffin solvents and cycloparaffin solvents, or a mixture of at least 2 kinds thereof. As commercial products of n-paraffin solvents, isoparaffin solvents, cycloparaffin solvents or a mixture thereof, for example, preferable ones are Isopar G. Isopar H, Isopar L. Isopar M and Exxsol D130, and Exxsol D140 (all of them, manufactured by Exxon Chemical Corporation), Shellsol 71 (manufactured by Shell Sekiyu K.K.), IP Solvent 1620, IP Solvent 2080 and IP Solvent 2835 (all of them, manufactured by Idemitsu Kosan Co., Ltd.), Moresco White P-40, Moresco White P-55 and Moresco White P-80 (all of them, manufactured by Matsumura oil Co., Ltd.), Liquid paraffin No. 40-S and Liquid paraffin No. 55-S (all of them, manufactured by Chuokasei Co., Ltd.).

[0017] The pigment dispersant used in the present invention is at least one pigment dispersant selected from the group consisting of the above-described modified novolak resin (A) and copolymer (B), which is solved in an electrically insulating hydrocarbon solvent.

[0018] Additionally, the above-described copolymer (B) has a relatively large side chain shown by the general formula (2) hanging down from the main chain, and such structure is observed in a graft copolymer. From such point, the copolymer (B) is referred to as graft copolymer (B) in the present specification.

[0019] First, the above-described modified novolak resin (A) is explained.

[0020] As a novolak resin to obtain the modified novolak resin (A), a novolak resin which is derived from monovalent phenols or multivalent phenols such as di or trioxybenzene and aldehydes can be used. As the monovalent phenols, there can be used unsubstituted phenols or alkyl-substituted phenols such as phenol, cresol, xylenol, trimethylphenol, propylphenol, butylphenol, amylhenol, hexylphenol, octylphenol, nonylphnol and dodecylphenol; or phenols having aromatic substituents such as monohydroxydiphenylmethane and phenylphenol. As the multivalent phenols, di or trihydroxybenzenes such as catechol, resorcinol, hydroquinone and trihydroxybenzene; or the alkyl-substituted or aromatic-substituted ones thereof. Further, dihydroxydiphenylmethanes of bisphenol A or bisphenol F, and dihydroxybiphenyls can also be used. Halogen-substituted phenols of the above-described phenols can also be used, for example, chlorinated or brominated phenols can be listed. These phenols can be used alone or in mixture of at least 2 kinds thereof.

[0021] Regarding the phenols, from the point of reactivity, phenols substituted by one alkyl group at the meta position are preferable as monovalent phenols, and resorcinol is preferable as multivalent phenols.

[0022] As aldehydes, one used generally in production of a novolak resin can be used without limitation in particular. Specifically, there are listed lower aliphatic aldehydes such as formaldehyde, paraformaldehyde, trioxane, cyclic formals, acetaldehyde, propionaldehyde, n-butylaldehyde, isobutylaldehyde and glyoxal; and aromatic aldehydes such as furfural and phenylaldehyde. These aldehydes can be used alone or in mixture of at least 2 kinds thereof.

[0023] To synthesize a novolak resin, according to a common method, these phenols and aldehydes may be reacted at 80 to 130°C in the presence of an acid catalyst such as p-toluenesulfonic acid, perchloric acid, hydrochloric acid, nitric acid, sulfuric acid, chloroacetic acid, oxalic acid and phosphoric acid. The reaction can be traced by a gel permeation chromatography (GPC) through measuring molecular weights.

[0024] Other than this method, a novolak resin may be synthesized by a method using a phenol derivative having a hydroxymethyl group like saligenin, or phenol derivative having a halogenated methyl group like o-chloromethylphenol.

[0025] Next, according to a common method, a novolak resin is reacted with epichlorohydrin or β-methylepichlorohydrin to obtain a novolak resin having an epoxy group. Obviously, a commercial novolak resin having an epoxy group can also be used.

[0026] Finally, a target modified novolak resin (A) is obtained by reacting a novolak resin having an epoxy group with carboxylic acids or amines described later. This reaction may use a solvent if necessary, use a catalyst such as an aliphatic amine, an aromatic amine and ammonium salt if necessary, and it can be carried out by heating at 60 to 160°C. The progress of reaction can be traced by GPC through measuring molecular weights or by measuring epoxy equivalents.

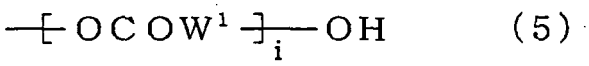
[0027] As described above, in addition to a method that modification is carried out after synthesis of a novolak resin, first, an aromatic hydroxyl group of the foregoing monovalent phenol or multivalent phenol is reacted with epichlorohydrin or β-methylepichlorohydrin to form a glycidyloxy group or 2,3-epoxy-2-methylpropyloxy group, which is reacted with carboxylic acids or amines described later, new phenols are added thereto if necessary, which is subjected to novolak

resinification reaction using aldehydes, thereby a modified novolak resin (A) can be obtained.

[0028] A group shown by the general formula (1) in a modified novolak resin (A) can be obtained by reacting an aromatic hydroxyl group with epichlorohydrin or β-methylepichlorohydrin, then, by reacting the resultant product with a hydroxycarboxylic acid of carbon numbers of 2 to 20 that may have an unsaturated bond or a branched structure, or the mixture thereof or the polycondensate thereof.

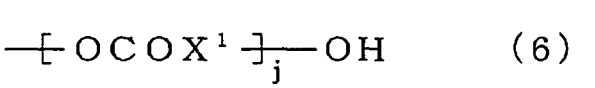
[0029] In the general formula (1), an oxygen atom at the far left is derived from an oxygen atom contained in an aromatic hydroxyl group of a novolak resin, W^1 and X^1 represent a divalent hydrocarbon group with carbon numbers in a range of 1 to 19 that may have an unsaturated bond and/or a branched structure, and R^1 represents a hydrogen atom or a methyl group.

[0030] In the general formula (1), a general formula (5):



(5)

wherein W^1 and i are the same as described above, and a general formula (6):



(6)

wherein X^1 and j are the same as described above, these groups can be derived from a hydroxycalboxylic acid with carbon numbers in a range of 2 to 20 that may have an unsaturated bond and/or a branched structure, or the mixture thereof or the polycondensate thereof.

[0031] As the above-described hydroxycalboxylic acid, there are listed glycolic acid, lactic acid, oxybutyric acid, hydroxyvaleric acid, hydroxycaproic acid, hydroxycaprylic acid, hydroxycapric acid, hydroxylauric acid, hydoxymyristic acid, hydroxypalmitic acid, ricinoleic acid, caster oil fatty acid, and their hydrogenated products and 12-hydroxysteraric acid. Above all, hydroxycalboxylic acid with carbon numbers in a range of 12 to 20 is preferred, particularly preferably, hydroxycalboxylic acid with carbon numbers in a range of 16 to 20 such as ricinoleic acid, caster oil fatty acid, and their hydrogenated products, and 12-hydroxystearic acid can be preferably used.

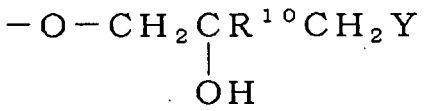
[0032] Repeating number i represents an integer in a range of 1 to 30, and j represents an integer in a range of 1 to 30. However, a suitable value depends on the kind of pigment used, specific surface area and particle diameter of pigment particle, properties of pigment surface treating agent, the kind of thermoplastic resin, and polarity of dispersant, it needs to select the optimum value according to each case. However, generally, i or $j \geq 2$, and $I + j \geq 2$ are preferred. When i or j exceeds the above-described range, dispersibility cannot be improved any more.

[0033] In the general formula (1), formation of a group shown by the general equation (5) or the general formula (6), for example, can be made by a method that a polyester is synthesized by polycondensation of a hydroxycarboxylic acid beforehand, and the terminal carboxylic group is reacted with the aforementioned epoxy group; or by a method that a carboxyl group of a hydroxycarboxylic acid is reacted with the aforementioned epoxy group, then further, the hydroxycarboxylic acid is polycondensated.

[0034] The above-described polycondensation reaction of the hydroxycarboxylic acid can be done by heating a reaction system at 180 to 220°C and stirring in the presence of, or without the presence of a catalyst such as p-toluenesulfonic acid, stannous octylate, dibutyltin diacetate, and tetra-n-butyl titanate, while water generated is removed by azeotropic solvents such as toluene and xylene. The reaction can be traced by GPC through measuring molecular weights or by measuring acid values.

[0035] The modified novolak resin (A) must have a group shown by the general formula (1) in a molecule. The number of the groups in the general formula (1) is preferably 1 to 20. A sufficient dispersion is not obtained when there is no this group. When the number of the groups exceeds the above-described range, although the effect can be attained, it becomes very difficult to control the molecular weight of a novolak resin having a larger number of a phenolic ring necessary for that, so that 20 is practically an upper limit. However, a suitable value depends on the kind of pigment used, specific surface area and particle diameter of pigment particle, presence or property of pigment surface treating agent, the kind of thermoplastic resin, and polarity of dispersant, it needs to select the optimum value according to application.

[0036] Moreover, the modified novolak resin (A) may further have in a molecule a group shown by a general formula (7):



(7)

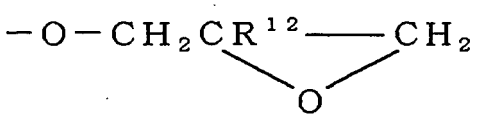
wherein an oxygen atom at the far left is derived from an oxygen atom contained in an aromatic hydroxyl group of a novolak resin, Y represents a monovalent organic group with carbon numbers in a range of 1 to 20 having an oxygen atom or a nitrogen atom at the terminal position (except the group shown by the general formula (5)) and R^{10} represents a hydrogen atom or a methyl group.

[0037] The group shown by the general formula (7) can be obtained by reacting an aromatic hydroxyl group with epichlorohydrin or β-methylepichlorohydrin, followed by reacting with monovalent carboxylic acids or monovalent amines. Additionally, a basic group formed by the reacting monovalent amines tends to affect an adverse influence on charging characteristics, hence, it is preferable not to use monovalent amines. In the case of using monovalent amines, it is necessary to pay attention on the amount used.

[0038] As concrete examples of the monovalent carboxylic acids, there can be used saturated acids such as acetic acid, propionic acid, butyric acid,caproic acid, caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid and stearic acid; unsaturated acids such as oleic acid, elaidic acid, linoleic acid, linolenic acid, arachidonic acid and eleostearic acid; and their hydrogenated acids.

[0039] As the monovalent amines, there can be used aliphatic primary monoamines such as methylamine, ethylamine, propylamine, butylamine, amylamine, octylamine, dodecylamine, stearylamine and benzylamine; aromatic primary monoamines such as aniline and naphthylamine, and their N-monoalkyl-substituted secondary monoamines; alkanol monoamines having a primary or secondary amino group such as ethanolamine, N-monoalkylethanolamine and diethanolamine.

[0040] Moreover, the modified novolak resin (A) may further have in a molecule a group shown by a general formula (8) and an aromatic hydroxyl group:



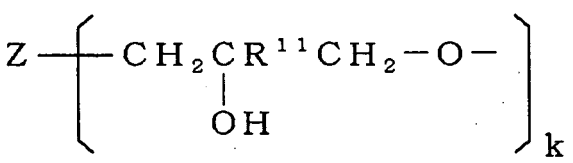
(8)

wherein an oxygen atom at the far left is derived from an oxygen atom contained in an aromatic hydroxyl group of a novolak resin, and R^{12} represents a hydrogen atom or a methyl group.

[0041] This means that a glycidyloxy group, 2,3-epoxy-2-methylpropyloxy group or aromatic hydroxyl group may be remained. However, it is not preferable for a modified novolak resin (A) to have both the group shown by the general formula (8) and an aromatic hydroxyl group. When it contains both, there is a tendency of generating gel.

[0042] There is no problem when the number of groups of a group shown by the general formula (7), a group shown by the general formula (8) and an aromatic hydroxyl group is each in a range of 0 to 19. When it exceeds this range, although the effect is attained, from the points that it becomes very difficult to control the molecular weight of a novolak resin with large functional group number and also at least one group shown by the general formula (1) must be present, 19 is practically the respective upper limits. However, a suitable value depends on the kind of pigment used, specific surface area and particle diameter of pigment particle, presence or property of pigment surface treating agent, the kind of thermoplastic resin, and polarity of dispersant, it is preferable to select the optimum value according to application.

[0043] The modified novolak resin (A) may be further substituted with a crosslinking group intermolecular or within a molecule shown by a general formula (9):



(9)

wherein an oxygen atom at the far right is derived from an oxygen atom contained in an aromatic hydroxyl group of the same molecule or different molecules of a novolak resin, Z represents an organic group of 2 to 6 functionalities with carbon numbers in a range of 1 to 40 having an oxygen atom or nitrogen atom at the terminal position, k represents an integer in a range of 2 to 6, and R^{11} represents a hydrogen atom or a methyl group.

[0044] To substitute an active hydrogen of an aromatic hydroxyl group by a crosslinking group intermolecular or within a molecule shown by the general formula (9), an aromatic hydroxyl group may be reacted with epichlorohydrin or β-methylepichlorohydrin, thereafter, which may be reacted with carboxylic acids of 2 to 6 functionalities, amines (including primary monoamine) or amino acids. Additionally, since a basic group formed by reacting amines or amino acids tends to affect an adverse influence on charging characteristics, it is preferable not to use amines or amino acids. In the case of using amines or amino acids, it is necessary to pay attention to the amount used.

[0045] As concrete examples of the multifunctional carboxylic acid, there can be used aliphatic polycarboxylic acids such as succinic acid, maleic acid, itaconic acid, cyclohexane dicarboxylic acid, adipic acid, azelaic acid, sebacic acid, 1,10-decanedicarboxylic acid, dodecenylsuccinic acid, dimer acid, 3,6-endomethylenetetrahydrophthalic acid, and 3,6-methylendomethylenetetrahydrophthalic acid; and aromatic polycarboxylic acids such as phthalic acid, isophtahlic acid, terephthalic acid, trimellitic acid, pyromellitic acid, benzophenonetetracarboxylic acid, ethyleneglycol bistrimellitate, and glycerol tristrimellitate.

[0046] As concrete examples of the multifunctional amines, there are listed ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethelenepentamine, pentaethylenehexamine, propylenediamine, (dimethylamino)propylamine, (diethylamino)propylamine, hexamethylenediamine, hexamethylenetriamine, N,N-bis(aminopropyl)methylamine, isophoronediamine, norbornanediamine, diaminodicyclohexylmethane, N-(aminoethyl)piperazine, N,N'-bis(aminoethyl)piperazine, xylylenediamine and dimer diamine; and aromatic polyamines such as melamine, benzoguanamine, m-phenylenediamine and diaminodiphenylmethane.

[0047] Further, polyetherdiamine, N-aminoethylethanolamine, or so-called polyaminoamide can also be used.

[0048] Further, a crosslinked structure can be formed by reacting an epoxy group with a primary amino group of two functionalities. In this case, the foregoing primary monoamine can also be used.

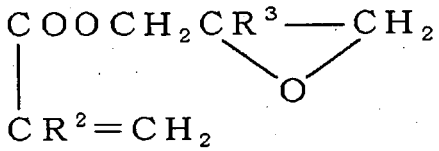
[0049] Amino acids such as leucine and threonine can also be used.

[0050] The above-described reaction can be carried out by heating at 60 to 160°C using a suitable organic solvent if necessary, and using a catalyst if necessary such as an aliphatic tertiary amine, an aromatic tertiary amine and an ammonium salt of a tertiary amine. The progress of reaction can be traced by GPC through measuring molecular weights or by measuring epoxy equivalents.

[0051] It is very difficult to control molecular weight of a novolak resin having a larger number of a phenolic ring, so it is preferable that the sum of aromatic hydroxyl groups of a modified novolak resin (sum of unsubstituted and substituted aromatic hydroxyl groups, the same below) is at most 20.

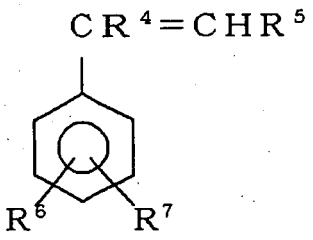
[0052] Next, the above-described graft copolymer (B) is explained.

[0053] The graft copolymer (B) can be obtained through reaction in a common method: (I) by using 10 to 90 mol% of an epoxy group-containing ethylenically unsaturated monomer shown by a general formula (10):



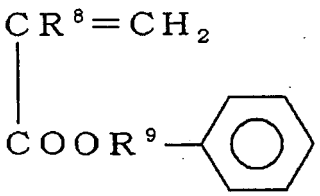
(10)

wherein R^2 and R^3 are the same as described above, and using 10 to 90 mol% of a monomer shown by a general formula (11):



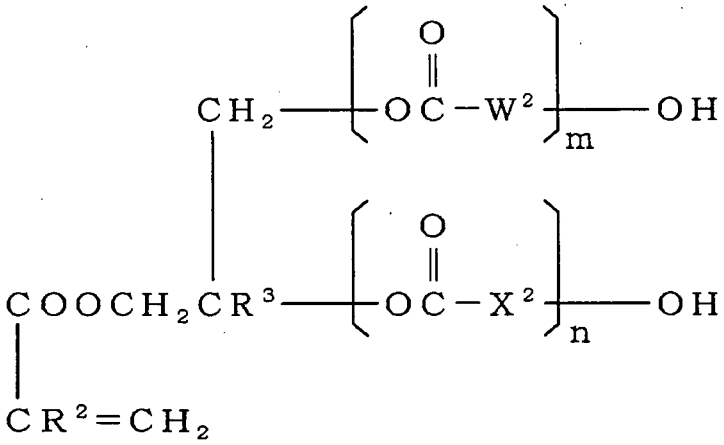
(11)

wherein R^4, R^5, R^6 and R^7 are the same as described above, and/or, 10 to 90 mol% of a monomer shown by a general formula (12):



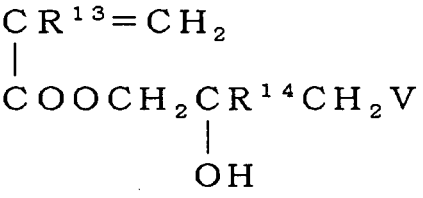
(12)

wherein R^8 and R^9 are the same as described above, according to need, using 0 to 80 mol% of other ethylenically unsaturated monomer having no functional group with high reactivity to an epoxy group, and a radical polymerization initiator such as peroxide and azo compounds, after obtaining a copolymer containing an epoxy group is obtained by a common method, followed by reacting an epoxy group of said copolymer with a hydroxycarboxylic acid, if necessary, carboxylic acids and amines; or (II) by using 10 to 90 mol% of a monomer shown by a general formula (13):



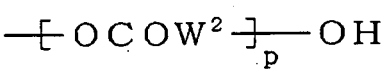
(13)

wherein R^2, R^3, W^2 and X^2 are the same as described above, m and n each independently represent an integer of m = 1 to 30, n = 0 to 30, and if necessary, by a general formula (14):



(14)

wherein, V is a monovalent organic group with carbon numbers in a range of 1 to 20 at the terminal positions, however, excluding the group shown by a general formula (15):

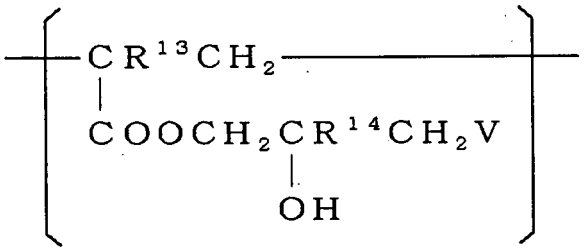


(15)

wherein W^2 and p are the same as described above, R^{13} and R^{14} each independently represent a hydrogen atom or a methyl group, and using 10 to 90 mol% of the monomer shown by the general formula (11) and/or the general formula

(12), according to need, using 0 to 80 mol% of other ethylenically unsaturated monomer having no functional group with high reactivity to an epoxy group, and a radical polymerization initiator such as peroxide and azo compound.

[0054] Additionally, an epoxy group of the copolymer obtained in the above-described method (I) is reacted with carboxylic acids or amines described later; a reaction to obtain a structural unit shown by the general formula (2) and a general formula (16):



(16)

wherein V, R^{13} and R^{14} are the same as described above, or a reaction to obtain a monomer shown by the general formula (13) and the general formula (14) by reacting an epoxy group of epoxy group containing ethylenically unsaturated monomer shown by the general formula (10) in the above-described method (II) with a hydroxycalboxylic acid, according to need, with carboxylic acids or amines, uses a solvent according to need, or uses an aliphatic amine, an aromatic amine or an ammonium salt according to need, and it can be conducted by heating at 60 to 160°C.

[0055] In the recurring unit shown by the above-described general formula (3), a chlorine atom is listed as a halogen atom represented by R^5. As a hydrocarbon group with carbon number 1 to 5 represented by R^6 or R^7, for example, there are listed alkyl groups such as methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, t-butyl and pentyl; as an alkoxy group with carbon numbers of 1 to 5, for example, methoxy and butoxy are listed, as an aryloxy group with carbon numbers of 6 to 10, for example, phenoxy is listed, and as a halogen atom, for example, a fluorine atom, a chlorine atom and a bromine atom are listed.

[0056] Regarding monomers used in production of the graft copolymer (B), as styrene derivatives among monomers shown by the general formula (11), there can be used an alkyl- substituted styrene such as vinyl toluene, α-methylstyrene, dimethylstyrene, ethylstyrene, isopropylstyrene and t-butylstyrene; a halogen-substituted styrene such as chlorostyrene, dichlorostyrene, bromostyrene and fluorostyrene; an alkoxy-substituted styrene such as methoxystyrene and butoxy-styrere; an aryloxy-substituted styrene such as phenoxystyrene; and β-chlorostyrene.

[0057] As the monomer shown by the general formula (12), benzyl (meth)acrylate and phenyl (meth)acrylate are listed.

[0058] As the epoxy group containing ethylenically unsaturated monomer shown by the general formula (10), glycidyl (meth)acrylate, and 2,3-epoxy-2-methylpropyl (meth)acrylate can be used.

[0059] As other ethylenically unsaturated monomer having no functional group with high reactivity to an epoxy group used according to need, there can be used an ethylenically unsaturated monomer having no functional group with high reactivity to an epoxy group such as a carboxyl group, a phenolic hydroxyl group, a primary amine and a secondary amine. For example, there can be listed alkyl esters of (meth)acrylic acid such as methyl (meth)acrylate, ethyl (meth) acrylate, propyl (meth)acrylate, butyl (meth)acrylate, cyclohexyl (meth)acryate, 2-ethylhexyl (meth)acrylate, octyl (meth) acrylate, lauryl (meth)acrylate, dodecyl (meth)acrylate, cetyl (meth)acrylate, stearyl (meth)acrylate, behenyl (meth)acrylate and norbornyl (meth)acrylate; (meth)acrylates having a cyclic ether group such as tetrahydrofurfuryl (meth) acrylate; (meth)acrylates having an aliphatic hydroxyl group such as 2-hydroxyethyl (meth)acrylate; (meth)acrylates having tertiary amino group such as dimethylaminoethyl (meth)acrylate and diethylaminoethyl (meth)acrylate; vinyl ethers such as methyl vinyl ether, dodecyl vinyl ether and propenyl ether propylene carbonate; vinyl ethers having an aliphatic hydroxyl group such as hydroxybutyl vinyl ether; and allyl esters of various acids such as allyl acetate.

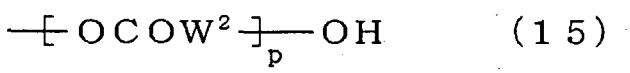
[0060] Additionally, in the case where a graft copolymer is obtained by using a monomer shown by the general formula (13) or the general formula (14) being obtained by reacting an epoxy group containing ethylenically unsaturated monomer with a hydroxycalboxylic acid, according to need, with carboxylic acids and amines, there can be used an ethylenically unsaturated monomer having a functional group with high reactivity to an epoxy group, such as a carboxyl group, a phenolic hydroxyl group, a primary amine and a secondary amine.

[0061] The recurring unit shown by the general formula (2) in the graft copolymer (B) can be obtained from a recurring unit derived from an epoxy group containing ethylenically unsaturated monomer shown by the above-described (10) and a hydroxycarboxylic acid with carbon numbers with 2 to 20 that may have an unsaturated bond or a branched structure, their mixture or the polycondensate. Alternatively, it can be derived from a monomer shown by the general formula (13) obtained from an epoxy group containing ethylenically unsaturated monomer shown by the above-described (10) and hydroxycarboxylic acid with carbon numbers with 2 to 20 that may have an unsaturated bond or a branched

structure, the mixture or the polycondensate thereof.

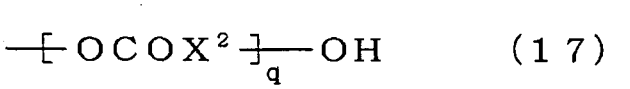
[0062] In the general formula (2), W^2 and X^2 represent a divalent hydrocarbon group with carbon numbers in a range of 1 to 19 that may have an unsaturated bond and/or a branched structure, R^2 and R^3 each independently represent a hydrogen atom or a methyl group.

[0063] In the general formula (2), a group shown by a genera 1 formula (15):



(15)

wherein W^2 and p are the same as described above, and by a genera 1 formula (17):



(17)

wherein X^2 and q are the same as described above, can be derived from a hydroxycarboxylic acid with carbon numbers in a range of 2 to 20 that may have an unsaturated bond and/or a branched structure, the mixture or the polycondensate thereof.

[0064] As the above-described hydroxycarboxylic acid, there are listed glycolic acid, lactic acid, oxybutyric acid, hydroxyvaleric acid, hydroxycaproic acid, hydroxycaprylic acid, hydroxycapric acid, hydroxylauric acid, hydroxymyristic acid, hydroxypalmitic acid, recinoleic acid, caster oil fatty acid, and their hydrogenated products, and 12-hydroxystearic acid. Among them, a hydroxycarboxylic acid with carbon numbers in a range of 12 to 20 is preferred, particularly preferably, there can preferably used hydroxycarboxylic acids with carbon numbers in a rang of 16 to 20 such as recinoleic acid and a caster oil fatty acid and their hydrogenated products, and 12-hydroxystearic acid.

[0065] Repeating number p represents an integer in a range of 1 to 30, and q represents an integer in a range of 0 to 30. However, a suitable value depends on the kind of pigment used, specific surface area and particle diameter of pigment particle, properties of pigment surface treating agent, the kind of thermoplastic resin, and polarity of dispersant, it needs to select the optimum value according to application. However, generally, p or $q \geq 2$, and $p + q \geq 2$ are preferred. When p or q exceeds the above-described range, dispersibility cannot be improved any more.

[0066] Formation of a group shown by the genera 1 formula (15) or the general formula (17) in the general formula (2) can be done, for example, by a method that polyester is synthesized beforehand by polycondensation of a hydroxycarboxylic acid, whose terminal carboxyl group is reacted with the aforementioned epoxy group; or a method that a carboxylic group of a hydroxycarboxylic acid monomer is reacted with the aforementioned epoxy group, then, further polycondensated with a hydroxycarboxylic acid.

[0067] The polycondensation reaction of the above-described hydroxycarboxylic acid can be conducted by heating and stirring a reaction system at 180 to 220°C in the presence or without the presence of a catalyst such as p-toluenesulfonic acid, stannous octylate, dibutyltin diacetate and tetra-n-butyl titanate, while removing water generated by azeotropic solvents such as toluene and xylene. The reaction can be traced by GPC through measuring molecular weights or by measuring acid values.

[0068] The graft copolymer (B) must have a recurring unit shown by the general formula (2) and a recurring unit shown by the general formula (3) and/or the general formula (4). The content of these relative to the graft copolymer (B) is preferably the amount corresponding to at least 10 mol% of a recurring unit shown by the general formula (2) in the graft copolymer (B), above all, the amount corresponding to 10 to 90 mol%; and the amount corresponding to at least 10 mol% of at least one kind selected from recurring units shown by the general formula (3) and the general formula (4), above all, the amount corresponding to 10 to 90 mol%. Additionally, what is meant to contain the amount corresponding to at least 10 mol% of a recurring unit shown by the general formula (2) is that a graft copolymer is divided into recurring units derived from ethylenically unsaturated monomers, the recurring unit shown by the general formula (2) contains at least 10 mol% to the whole recurring units. Namely, in the case where a graft copolymer is obtained by copolymerization of n ethylenically unsaturated monomers, the number of recurring units shown by the general formula (2) in a molecule of said graft copolymer means at least 0.1 x n. Further, what is meant to contain the amount corresponding to at least 10 mol% of at least one kind selected from recurring units shown by the general formula (3) and the general formula (4) is that a graft copolymer is divided into recurring units derived from ethylenically unsaturated monomers, at least one kind selected from recurring units shown by the general formula (3) and the general formula (4) contains at least 10 mol%. Namely, in the case where a graft copolymer is obtained by copolymerization of n ethylenically unsaturated monomers, the number of recurring units of at least one kind selected from recurring units shown by the general formula

(3) and the general formula (4) means at least 0.1 x n.

[0069] When either the recurring unit shown by the general formula (2) or at least one kind of recurring unit selected from recurring units shown by the general formula (3) and the general formula (4), or both do not contain the amount corresponding to a predetermined mol, sufficient dispersibility cannot be obtained. However, a suitable value depends on the kind of pigment used, specific surface area and particle diameter of pigment particle, presence or property of pigment surface treating agent, the kind of thermoplastic resin, and polarity of dispersant, it is preferable to select the optimum value according to application.

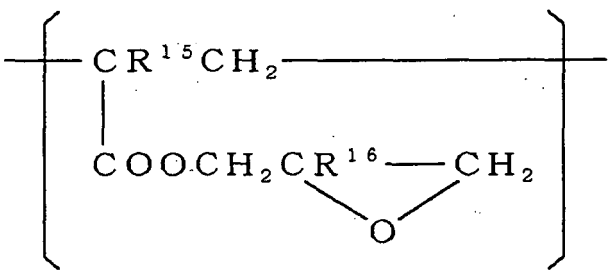
[0070] Further, the graft copolymer (B) may have a recurring unit shown by a general formula (16).

[0071] The recurring unit shown by the general formula (16) can be obtained by reacting an epoxy group containing ethylenically unsaturated monomer or an epoxy group of copolymer with monovalent carboxylic acids or monovalent amines. Additionally, a basic group formed by reacting monovalet amines tends to affect an adverse influence on charging characteristics, hence, it is preferable not to use monovalent amines. In the case of using monovalent amines, it is necessary to pay attention to the amount used.

[0072] As concrete examples of the monovalent carboxylic acids, there can be used saturated fatty acids such as acetic acid, propionic acid, butyric acid, caproic acid, caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid and stearic acid; and unsaturated acids such as oleic acid, elaidic acid, linoleic acid, linolenic acid, arachidonic acid and eleostearic acid.

[0073] As the monovalent amines, there can be used aliphatic primary monoamines such as methylamine, ethylamine, propylamine, butylamine, amyl amine, octylamine, docecylamine, stearylamine, benzylamine; aromatic primary monoamines such as aniline and naphthylamine, and secondary monoamines of these by N-monoalkyl substitution; and alkanolmonoamines having a primary or secondary amino group such as ethanolamine, N-monoalkylethanolamine and diethanolamine.

[0074] Further, the graft copolymer (B) may have a recurring unit shown by a general formula (18):



(18)

wherein R^{15} and R^{16} each independently represent a hydrogen atom or a methyl group.

[0075] This means that a glycidyloxy group or a 2,3-epoxy-2-methylpropyloxy group in an epoxy group containing ethylenically unsaturated monomer may remain intact.

[0076] The above-described graft copolymer (B) has a weight-average molecular weight of 3000 to 100000. When the weight-average molecular weight is less than the above-described range, although dispersibility is sufficient, it is difficult to adjust polymerization, whereas when it exceeds the above-described range, sufficient dispersibility tends to be difficult to obtain.

[0077] In the present invention, in a system where an electrically insulating hydrocarbon solvent is used as a solvent, by using the above-described specific pigment dispersant, a liquid developing agent with high solid content concentration having excellent dispersion stability and redispersibility can be obtained without lowering the electric resistance value (volume resistivity).

[0078] The amount of pigment dispersant used in the present invention is preferably 2 to 100 parts by mass relative to 100 parts by mass of colored chip obtained by heat kneading a pigment with a thermoplastic resin, more preferably 2 to 50 parts by mass. When the amount of pigment dispersant used is less than the above-described range, dispersibility and redispersibility tend to be lowered, whereas when it exceeds the above-described range, electric resistance value tends to be lowered.

[0079] As charge controlling agents used in the present invention according to need, they are broadly classified into two types of (1) and (2) which will be explained below.

(1) A type of comprising a substance capable of ionization or absorption of ion, thereby covering the surface of toner particle:

Preferable charge controlling agents of this type include fat such as linseed oil and soy oil, alkyd resin, a halogenated polymer, an aromatic polycarboxylic acid, an acid group-containing aqueous dye, and an oxidized condensate of an aromatic polyamine.

(2) A type of making coexistence by dissolving a substance capable of giving and receiving ions with a toner particle in an electrically insulating solvent:

Preferable charge controlling agents of this type include metal soap such as cobalt naphthenate, nickel naphthenate, iron naphthenate, zinc naphthenate, zirconium octylate, cobalt octylate, nickel octylate, zinc octylate, cobalt dodecanoate, nickel dodecanoate, zinc dodecanoate, and cobalt 2-ethylhexanoate; metal sulfonates such as petroleum metal sulfonate and metal sulfosuccinate; phospholipids such as lecithin and kephalin; metal salicylates such as t-butylsalicylic acid a metal complex; a polyvinylpyrolidone resin, a polyamide resin, a sulfonic acid-containing resin and a hydroxybenzoic acid derivative.

[0080] Next, a process for producing the liquid developing agent of the present invention is explained.

[0081] In the present invention, actually as long as a colored chip obtained by heat kneading of pigment and thermoplastic resin is minutely powdered by wet pulverization, and dispersed in an electrically insulating solvent containing the above-described pigment dispersant, the kind of powdering machine and dispersing machine, a combination of powdering steps are not particularly limited. Herein, a simple production method with combination of both dry pulverization and wet pulverization of colored chip is explained.

[0082] First, the above-described pigment and thermoplastic resin are heat-kneaded by a three-roll mill, and a biaxial extruder, after being cooled, the resultant colored chip is dry-pulverized by a dry powdering machine. The coarse pulverized powder obtained by dry pulverization has preferably an average particle diameter of about 7 to 12 μm. Additionally, when the kneaded product subjected to dry pulverization is soft, for example, in the case of softening point of at most 100°C, it is cooled and embrittled with liquid nitrogen or solid carbon dioxide before pulverization. As the dry powdering machine, for example, there can be optionally used a hammer mill, a jet mill, a pin mill, a turbomill, a cutter mill and a ball mill.

[0083] Next, using a wet powdering machine, the above-described coarse pulverized powder by dry pulverization is subjected to wet pulverization in an electrically insulating solvent containing at least one pigment dispersant selected from the foregoing modified novolak resin (A) and the foregoing graft copolymer (B), the liquid developing agent of the present invention can be obtained thereby. Additionally, a charge controlling agent that can be added according to need may be added upon wet pulverization and/or after wet pulverization. As the above-described powdering machine, for example, there can be optionally used media-type powdering machines such as an Eiger mill, an atoreiter, a sand mill, a dinomill, a ball mill, DCP mill, an apex mill and a pearl mill; and media-free powdering machines such as Ultimizer (manufactured by Sugino Machine Ltd.), Nanomizer (manufactured by Nanomizer Inc.), Microfuldizer (manufactured by Mizuho Industrial Co., Ltd.) and DeBee 2000 (manufactured by Debee Corporation). The toner particle in a liquid developing agent obtained by wet pulverization preferably has an average particle diameter of 0.1 to 5 μm, more preferably 0.1 to 3 μm, from the point of obtaining a highly fine photographic image.

[0084] The liquid developing agent obtained from the materials and production method described above is a liquid developing agent capable of realizing high solid content having excellent developing properties as well.

[0085] For example, in the liquid developing agent of the present invention, the solid content concentration in the liquid developing agent is preferably 13 to 50 % by mass based on the whole solid components including the pulverized powder of colored chip (i.e., toner particle), pigment dispersant, and other solid content. By using wet pulverization method of colored chip being fundamentally difficult to maintain dispersion stability and charging characteristics, good flowability and developing property can be maintained up to 50 % by mass of solid content concentration, which can exhibit a nonconventional very great effect.

EXAMPLES

[0086] The liquid developing agent of the present invention will be described in detail with reference to Examples below. Additionally, unless otherwise noted, "part" and "%" mean "part by mass" and "% by mass", respectively.

[0087] The pigment, pigment dispersant and thermoplastic resin used in the following Examples and Comparative Examples are explained.

<Pigment>

[0088] Pigment blue 15:3 (manufactured by Dainichiseika Color & Chemicals Mfg. Co., Ltd.)

<Pigment dispersant 1 >

[0089] In a reactor was charged a mixture of 30 parts of an epoxy-modified novolak resin (manufactured by Japan Epoxy Resins Co., Ltd., Epicoat 154), 75 parts of a polyester with an acid value of 30 and weight-average molecular weight of 4500 obtained by polycondensation of 12-hydroxystearic acid, 35 parts of stearic acid and 0.2 parts of tetraethylamonium bromide, heated and stirred at 130 to 150°C under nitrogen atmosphere for 3 hours, then the catalyst was removed by vacuum filtration to give a modified novolak resin (pigment dispersant 1) with a weight-average molecular weight of 8000.

<Pigment dispersant 2>

[0090] To a reactor were added 100 parts of 12-hydroxystearic acid, 10 parts of xylene and 0.1 parts of tetra-n-butyl titanate, condensation reaction was conducted at 180 to 200°C while azeotropically distilling water generated out under nitrogen stream. Xylene was distilled out at a predetermined acid value, thereby to obtain a polyester of a light brown polymer having an acid value of 33 and weight-average molecular weight of 4400. Next, 74.3 parts of this polyester and 25.7 parts of a copolymer of styrene and glycidyl methacrylate as an epoxy-containing copolymer (respective contents; 80 mol% and 20 mol%) were reacted at 130 to 150°C in 40 parts of dimethylformamide as a solvent. From the measurement of acid value and an epoxy group, the solvent was distilled out under reduced pressure when the residual amount of a carboxylic acid and an epoxy group was not more than measuring limit, thereby to give a graft copolymer (pigment dispersant 2). The weight-average molecular weight by GPC measurement was 35000.

<Comparative pigment dispersant>

[0091] As a comparative pigment dispersant, Solsparse 17000 (Abesia Co., Ltd.) was used.

<Thermoplastic resin 1>

[0092] Epoxy resin (AER6064, manufactured by Asahi Kasei Corporation) was used.

<Thermoplastic resin 2>

[0093] 76.7 parts of styrene (St), 14.7 parts of stearyl methacrylate (SMA), 8.6 parts of dimethylacrylamide (DMAA), 160 parts of toluene and 1.5 parts of azobisisobutyronitrile as an initiator were mixed, radical reaction was conducted at 80°C for 10 hours. The resultant resin solution was further heated at 150°C for 8 hours under reduced pressure under the condition of 70 cmHg (about 93 kPa), toluene, unreacted monomers and low molecular oligomers were distilled out, thereby a thermoplastic resin 2 was obtained. The thermoplastic resin 2 obtained had the composition (St:SMA:DMAA=85:5:10 mole ratio), weight-average molecular weight of 45800 and a melting point of 92°C.

EXAMPLE 1

[0094] After cooling the milled product (colored chip) obtained by melt kneading of 250 parts of Pigment blue 15:3 and 750 parts of thermoplastic resin 1 at 140°C using a hot three-roll mill, it was pulverized using a jet mill (manufactured by Nippon Pneumatic Mfg. Co., Ltd.). Next, 140 parts of this coarse pulverized powder, 8.8 parts of pigment dispersant 1 and 551.2 parts of paraffin based solvent with a high boiling point (Moresco White P-40) were subjected to wet pulverization at 40°C for about 90 minutes using Eiger mill (trade name M-250) filled with zirconia beads of 0.5 mm diameter, thereby to give a liquid developing agent 1 with a solid content concentration of 21.3 %.

EXAMPLE 2

[0095] After cooling the milled product (colored chip) obtained by melt kneading of 250 parts of Pigment blue 15:3 and 750 parts of thermoplastic resin 1 at 140°C using a hot three roll mill, it was pulverized using a jet mill (manufactured by Nippon Pneumatic Mfg. Co., Ltd.). Next, 140 parts of this coarse pulverized powder, 5.3 parts of pigment dispersant 1 and 554.7 parts of paraffin based solvent with a high boiling point (Moresco White P-40) were subjected to wet pulverization at 40°C for about 90 minutes using Eiger mill (trade name M-250) filled with zirconia beads of 0.5 mm diameter, thereby to give a liquid developing agent 2 with a solid content concentration of 20.8 %.

EXAMPLE 3

[0096] After cooling the milled product (colored chip) obtained by melt kneading of 333 parts of Pigment blue 15:3 and 667 parts of thermoplastic resin 1 at 140°C using a hot three-roll mill, it was pulverized using a jet mill (manufactured by Nippon Pneumatic Mfg. Co., Ltd.). Next, 210 parts of this coarse pulverized powder, 5.3 parts of pigment dispersant 1 and 484.7 parts of paraffin based solvent with a high boiling point (Moresco White P-40) were subjected to wet pulverization at 40°C for about 90 minutes using Eiger mill (trade name M-250) filled with zirconia beads of 0.5 mm diameter, thereby to give a liquid developing agent 3 with a solid content concentration of 30.8 %.

EXAMPLE 4

[0097] After cooling the milled product (colored chip) obtained by melt kneading of 250 parts of Pigment blue 15:3 and 750 parts of thermoplastic resin 1 at 140°C using a hot three-roll mill, it was pulverized using a jet mill (manufactured by Nippon Pneumatic Mfg. Co., Ltd.). Next, 140 parts of this pulverized powder, 8.8 parts of pigment dispersant 2 and 551.2 parts of paraffin based solvent with a high boiling point (Moresco White P-40) were subjected to wet pulverization at 40°C for about 90 minutes using Eiger mill (trade name M-250) filled with zirconia beads of 0.5 mm diameter, thereby to give a liquid developing agent 4 with a solid content concentration of 21.3 %.

EXAMPLE 5

[0098] A liquid developing agent 5 with a solid content concentration of 21.3 % was obtained in the same manner as in Example 1 except that the thermoplastic resin 2 in place of the thermoplastic resin 1, and a paraffin based solvent with a high boiling point (IP Solvent 2835) in place of a paraffin based solvent with a high boiling point (Moresco White P-40) were used.

COMPARATIVE EXAMPLE 1

[0099] After cooling the milled product (colored chip) obtained by melt kneading of 250 parts of Pigment blue 15:3 and 750 parts of thermoplastic resin 1 at 140°C using a hot three-roll mill, it was pulverized using a jet mill (manufactured by Nippon Pneumatic Mfg. Co., Ltd.). Next, 140 parts of this coarse pulverized powder and 560 parts of a paraffin based solvent with a high boiling point (Moresco White P-40) were subjected to wet pulverization at 40°C for about 90 minutes using Eiger mill (trade name M-250) filled with zirconia beads of 0.5 mm diameter, thereby a liquid developing agent 6 with a solid content concentration of 20 % was obtained.

COMPARATIVE EXAMPLE 2

[0100] After cooling the milled product (colored chip) obtained by melt kneading of 250 parts of Pigment blue 15:3 and 750 parts of the thermoplastic resin 1 at 140°C using a hot three-roll mill, it was pulverized using a jet mill (manufactured by Nippon Pneumatic Mfg. Co., Ltd.). Next, 140 parts of this coarse pulverized powder, 8.8 parts of Solsperse 17000 (manufactured by Abecia Limited) and 551.2 parts of a paraffin based solvent with a high boiling point (Moresco White P-40) were subjected to wet pulverization at 40°C for about 90 minutes using Eiger mill (trade name M-250) filled with zirconia beads of 0.5 mm diameter, thereby a liquid developing agent 7 with a solid content concentration of 21.3 % was obtained.

<Evaluation>

[0101] The liquid developing agents 1 to 7 prepared in Examples 1 to 5 and Comparative Examples 1 to 2 were measured for a viscosity, an electric resistance value and a range of particle diameter. The results are shown in Table 1.

(Viscosity)

[0102] The viscosity of liquid developing agent at 25°C was measured as a viscosity after 60 seconds using an E-type viscometer (at 20 rpm for viscosity not less than 10 mPa·s but less than 100 mPa·s; 5 rpm for viscosity more than 100 mPa·s). Additionally, the viscosity of liquid developing agent of Comparative Example 1 was too high to measure.

(Electric resistance value)

[0103] The liquid developing agents (viscosity was able to be measured) were measured for an electric resistance

value by a R834 manufactured by Advance Corporation.

(Range of particle diameter)

[0104] The liquid developing agents were measured for the range of particle diameter of toner particles by eye using an optical microscope (manufactured by Olympus Corporation).

TABLE 1

	Viscosity (mPa·s)	Volume resistivity (Ω·cm)	Range of particle diameter (μm)
Ex. 1	16	6.0×10^{13}	1-2
Ex. 2	20	3.0×10^{14}	1-2
Ex. 3	100	5.0×10^{14}	1-2
Ex. 4	21	4.0×10^{13}	1-2
Ex. 5	50	5.0×10^{14}	1-2
Com. Ex. 1	-	-	>5
Com. Ex. 2	15	8.0×10^{12}	1-4

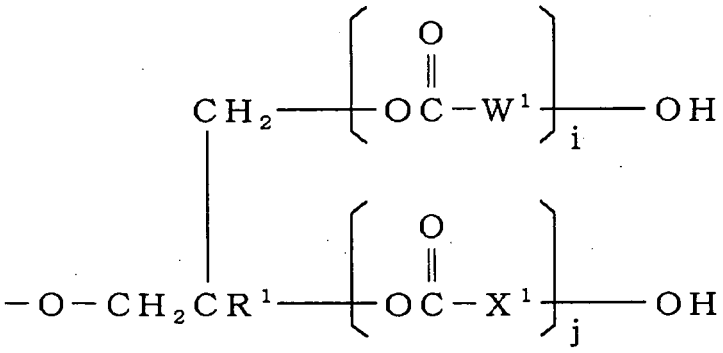
INDUSTRIAL APPLICABILITY

[0105] A liquid developing agent obtained by wet pulverization of a colored chip obtained by heat kneading a pigment with a thermoplastic resin using a specific pigment dispersant having an aromatic ring and a ring-opened structure of an epoxy group by a hydroxycarboxylic acid-derived carboxyl group has, in spite of wet pulverization method, a low viscosity being capable of realizing high solid content, further has a high electric resistance value and excellent developing properties.

Claims

1. A liquid developing agent where a colored chip obtained by heat kneading a pigment with a thermoplastic resin is dispersed by wet pulverization in an electrically insulating hydrocarbon solvent dissolving at least one pigment dispersant selected from the group consisting of the following modified novolak resin (A) and copolymer (B) having an aromatic ring and a ring-opened structure of an epoxy group by a hydroxycarboxylic acid-derived carboxyl group:

Modified novolak resin (A): a modified novolak resin having a novolak resin-derived aromatic ring and at least one group shown by a general formula (1) by ring-opening of an epoxy group by a hydroxycarboxylic acid-derived carboxyl group:

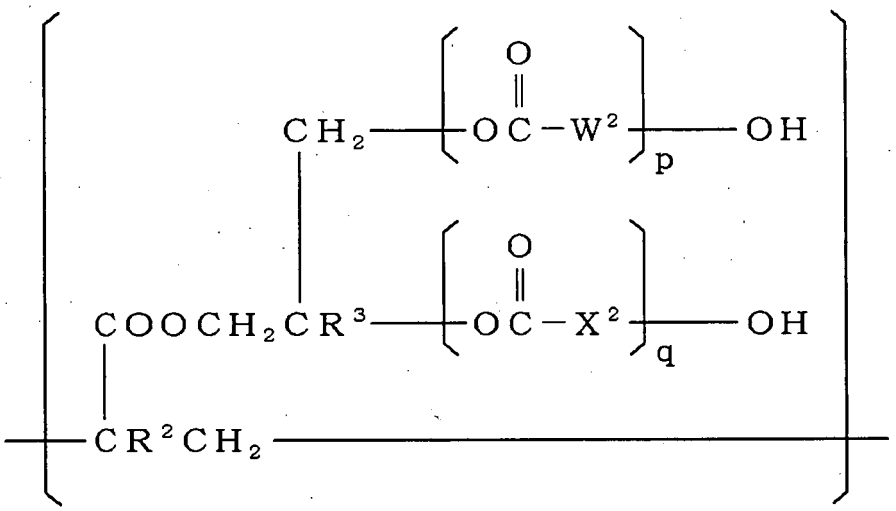


(1)

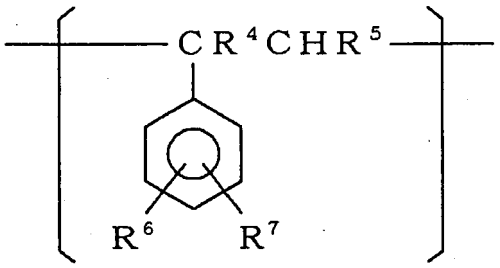
wherein an oxygen atom at the far left is derived from an oxygen atom contained in an aromatic hydroxyl group of a novolak resin, W^1 and X^1 each independently represent a divalent hydrocarbon group with carbon numbers of 1 to 19, i and j each independently represent an integer of i = 1 to 30 and j = 0 to 30, and R^1 represents a hydrogen atom or a methyl group.

Copolymer (B): a copolymer with a weight-average molecular weight of 3000 to 100000, having, in said copolymer, the amount corresponding to at least 10 mol% of the recurring unit shown by a general formula (2), and

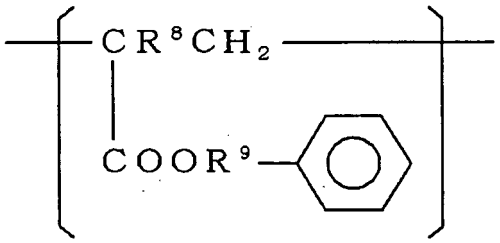
the amount corresponding to at least 10 mol% of at least one kind selected from the recurring units shown by a general formula (3) and a general formula (4):



(2)



(3)



(4)

wherein W^2 and X^2 each independently represent a divalent hydrocarbon group with carbon numbers of 1 to 19, p and q each independently represent an integer of p = 1 to 30, and q = 0 to 30, R^2, R^3 and R^4 each independently represent a hydrogen atom or a methyl group, R^5 represents a hydrogen atom or a halogen atom, R^6 and R^7 each independently represent a hydrogen atom, a hydrocarbon group with carbon numbers of 1 to 5, an alkoxy group with carbon numbers of 1 to 5, an aryloxy group with carbon numbers of 6 to 10, or a halogen atom, R^8 represents a hydrogen atom or a methyl group, and R^9 represents a direct bond or a methylene group.

2. The liquid developing agent of Claim 1, wherein the concentration of the total solid content in a liquid developing agent was 13 to 50 % by mass.

3. The liquid developing agent of Claim 1 or 2, wherein the composition of the pigment dispersant is 2 to 100 parts by mass relative to 100 parts by mass of the colored chip.

4. The liquid developing agent of any one of Claims 1 to 3, wherein said electrically insulating hydrocarbon solvent is a high boiling point paraffin solvent.

5. A process for producing the liquid developing agent of any one of Claims 1 to 4, wherein the colored chip obtained by heat kneading a pigment with a thermoplastic resin is subjected to dry pulverization into a coarse pulverized powder beforehand, further, said coarse pulverized powder is subjected to wet pulverization in an electrically insulating hydrocarbon solvent dissolving at least one pigment dispersant selected from the group consisting of said modified novolak resin (A) and said copolymer (B).

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2006/310311

A. CLASSIFICATION OF SUBJECT MATTER
G03G9/13(2006.01)

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
G03G9/13

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2006
Kokai Jitsuyo Shinan Koho 1971-2006 Toroku Jitsuyo Shinan Koho 1994-2006

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	JP 2004-21023 A (Sakata Inx Corp.), 22 January, 2004 (22.01.04), Claim 1; Par. Nos. [0135] to [0147] (Family: none)	1,4 1-5
Y	JP 2002-139871 A (Sakata Inx Corp.), 17 May, 2002 (17.05.02), Claim 1; Par. Nos. [0124] to [0126] (Family: none)	2-3
Y	JP 2002-287433 A (Sakata Inx Corp.), 03 October, 2002 (03.10.02), Par. Nos. [0016] to [0023], [0032] to [0037] (Family: none)	2-3

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
07 July, 2006 (07.07.06)	18 July, 2006 (18.07.06)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2006/310311

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 3-188469 A (Fuji Photo Film Co., Ltd.), 16 August, 1991 (16.08.91), Page 30, lower left column, line 14 to page 31, lower left column, line 14 (Family: none)	5
Y	JP 4-85551 A (Fuji Photo Film Co., Ltd.), 18 March, 1992 (18.03.92), Page 17, upper right column, line 9 to page 18, upper right column, line 5 (Family: none)	5

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 60021056 A **[0004]**
- JP 5134468 A **[0004]**