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(54) Liquid developer and method for preparing the same

(57) A liquid developer is provided which includes toner particles, a non-aqueous medium for dispersing the toner particles and a charge-imparting polymer present in the vicinity of the toner particle surface. The charge-imparting polymer contains a polar group comprising at least one of acid and basic groups for imparting charges to the toner particles. Its swelling degree relative to the non-aqueous medium is equal to or greater than 0.5 g.

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Description

BACKGROUND OF THE INVENTION

Field Of The Invention

The present invention relates to a liquid devoloper useful for developing electrostatic latent images in an electrophotographic process.

Description Of Related Art

In the electrophotographic process, two general categories of processes are known for developing electrostatic latent images; wet and dry development processes.

The dry development process involves spreading colorant powders over electrostatic latent images for attachment thereto. It advantageously provides good handling characteristics as well as toner storage stability. In recent years, there has been a need for high-quality images with high resolution in such applications as video printing and the others. Such high resolution can be attained by reducing a particle diameter of liquid developers. However, in the dry development process, the size reduction of toner particles in diameter disadvantageously results in flocculation of toner particles, non-uniform distribution of charge amounts as well as poor cleaning characteristics.

The wet development process utilizes liquid developers including, as a colorant, a dye and/or pigment dispersed in an electrical insulating medium, and is capable of utilizing toner particles having a smaller particle diameter relative to that used in the dry development process. This results in high resolution and gradation of the developed images.

Liquid developers generally include an electrical insulating medium, such as petroleum hydrocarbons, having a volume resistivity equal to or greater than 10^9 Ωcm and a dielectric constant not exceeding 3.5; a colorant such as carbon black and phthalocyanines; toner particles prepared integrally with or separately from the colorant for fixing the developed images; and a dispersion stabilizer for helping disperse the particles in the medium and for stabilizing the dispersed particles against flocculation.

In order for such liquid developers to be effective, sufficient amounts of charge must be imparted to the toner particles. The use of polymer containing a polar group, such as an ethylene-methacrylate acid copolymer, to prepare electrically charged toner particles is known in the art.

However, the toner particles obtained from the ethylene-methacrylate copolymer exhibit poor dissociation in the medium and accordingly generate a low level of charge amount so that a high degree of image density can not be obtained.

It is known in the art to add a charge director that is soluble in the medium for the purpose of increasing the charge amount of the toner particles. A variety of compounds are employed as such a charge director. The known charge directors include anionic glycerides, lecithin, metallic soap, and BASIC BARIUM PETRONATE (product name). Another known liquid developer contains therein, as a charge adjuvant, metallic salts of hydroxycarboxylic acid such as aluminium hydroxycarboxylates (see, for example, Japanese Patent Laying-open No. Hei 6-236074 (1994)).

It is also known in the art to add a high-molecular surface active agent for its adsorption onto toner particle surfaces so that an increased amount of charge is imparted to the toner particles (see, for example, Japanese Patent Laying-open No. Hei 5-188655 (1993)).

However, the charge director and high-molecular surface active agent, as employed in the above-described conventional techniques to increase the charge amount of the toner particles, are both soluble in the medium so that certain portions thereof dissolve in the medium and remain there in their dissolved form while the other portions are left adsorbed onto the toner particle surfaces. As increasing amounts of those compounds are added to the medium, the volume resistivity of the liquid developer accordingly decreases to cause "fogging". Poor reproducibility of halftone dots or fine lines also results. The resulting limitations imposed upon the amounts of those compounds to be added render them ineffective to impart the adequate amount of charge to the toner particles.

SUMMARY OF THE INVENTION

The present invention is directed toward solving the above-described conventional problems.

It is accordingly an object of the present invention to provide a liquid developer which is capable of increasing charge amounts of toner particles to thereby result in high density and good resolution of developed images.

The present invention provides a liquid developer which includes a non-aqueous medium, toner particles dispersed in the non-aqueous medium, and a charge-imparting polymer present in the vicinity of the toner particle surface. The degree of swelling of the charge-imparting polymers relative to the non-aqueous medium is equal to or greater than 0.5 g. The charge-imparting polymers contain a polar group comprising at least one of acid and basic groups for imparting charges to the toner particles.

The Charge-Imparting Polymers

[Degree of Swelling]

A degree of swelling of the charge-imparting polymer employed for the present invention is equal to or greater than 0.5 g, preferably equal to or greater than 1.0 g relative to a non-aquesou medium. An excessively reduced degree of its swelling relative to the non-aquesous medium possibly results in failure to impart a relatively larger amount of charge to the toner particles. This more likely causes a reduced density of the resulting images. Although an upper limit of the swelling degree is not particularly specified, it must be within a measurable range.

The following procedure can be utilized to determine the degree of swelling in accordance with the present invention.

Added to 20 g of a first medium having a low dielectric constant for employment as a non-aqueous medium for a liquid developer is 1 g of the charge-imparting polymer. Subsequently added to the non-aqueous medium is a second medium which has a higher polarity relative to that of the first non-aqueous medium and is capable of dissolving the charge-imparting polymer, thereby forming a combined medium. The addition of the second medium having a relatively higher polarity is continued untill the charge-imparting polymer completely dissolves in the combined medium. The second medium having a relatively higher polarity is then removed from the combined medium such as by an evaporator to separate the charge-imparting polymer. The subsequent centrifuging thereof at 3,000 G for 30 minutes allows the charge-imparting polymer to precipitate. The precipitates are collected to measure a weight of the non-aqueous first medium contained in the precipitates and thereby determine a degree of swelling of the charge-imparting polymer. Thus, the term "degree of swelling" as used herein refers to a permissible weight of solvent constituting the non-aqueous to be contained in 1 g of the charge-imparting polymer.

[Polar Group]

The charge-imparting polymer employed for the present invention contains a polar group comprising at least one of acid and basic groups for imparting electrical charges to the toner particles. The charge-imparting polymer may contain both of the acid and basic groups if one of those groups is larger in amount relative to the other.

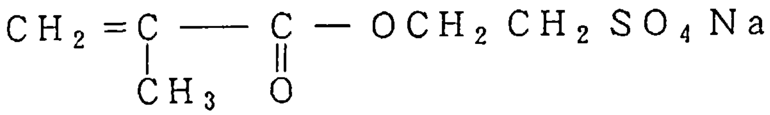
Any acid groups which are capable of producing an anionic group upon application of an electric field may be utilized. Specifically, the acid groups include -COOH, - SO_3Na, $-SO_3NH_4$, $-OPO(OH)_2$. Likewise, any basic groups which are capable of producing a cationic group uppon application of an electrical field may be utilized. The basic groups specifically include $-N(CH_3)_2$, $-N(C_2H_5)_2$, $-N^+(CH_3)_3Cl^-$.

The amount of the polar groups to be contained in the charge-imparting polymer may be suitably determined considering the predicted degree of the polymer swelling and charge amount to be imparted to the toner particles. In general, the amount of the polar groups preferably ranges from 0.1 to 10 millimoles, more preferably from about 0.5 to about 5 millimoles per gram of the charge-imparting polymer. As the amount of the polar groups contained in the charge-imparting polymer becomes excessively small, the decreasing amount of charge may be induced in the toner particles. On the other hand, as it goes excessively large, it becomes more difficult to bring the degree of polymer swelling within the above-stated range.

Any polymers which have a polar group may be utilized as the charge-imparting polymer in accordance with the present invention. For example, the charge-imparting polymer can be prepared by copolymerizing a first monomer having a polar group with a second monomer. Examples of the polar, first monomer are described below.

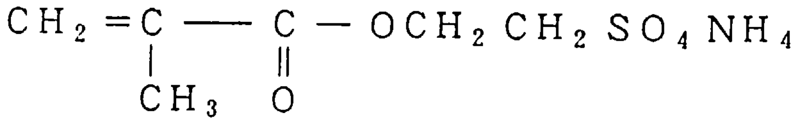
The monomers having an acid group include (meth)acrylic acid, ANTOX-MS-2N(product name; manufactured by Nippon Nyukazai Co., Ltd.; represented by the following chemical structural formula 1), ANTOX-MS-NH_4 (product name; manufactured by Nippon Nyukazai Co., Ltd.; represented by the following chemical structural formula 2).

Chemical structural formula 1



$$CH_2=\underset{\displaystyle CH_3}{\underset{|}{C}}-\underset{\displaystyle O}{\underset{\|}{C}}-OCH_2CH_2SO_4Na$$

Chemical structural formula 2



$$\mathrm{CH_2=\underset{\underset{CH_3}{|}}{C}-\underset{\underset{O}{\|}}{C}-OCH_2CH_2SO_4NH_4}$$

The monomers having a basic group include dimethylaminoethyl (meth)acrylamides, diethylaminoethyl (meth)acrylates, dimethylaminopropyl (meth)acrylamides, and quaternarized compounds thereof.

Any monomers which are well known in the art as being useful for radical polymerization may be employed as the second monomer to be copolymerized with the above polar, first monomer. Examples of useful second monomers include (meth)acrylates, polymerizable aromatic compounds, and hydroxyl-containing monomers.

The followings are examples of the above-mentioned (meth)acrylates: methyl acrylates, methyl methacrylates, ethyl acrylates, ethyl methacrylates, n-butyl acrylates, n-butyl methacrylates, isobutyl acrylates, 2-ethylhexyl acrylates, lauryl methacrylates, and phenyl acrylates.

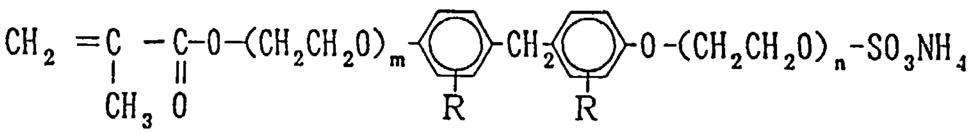
The followings are included as examples of the above-mentioned polymerizable aromatic compounds: styrenes, α-methyl styrenes, vinyl ketones, t-butyl styrenes, p-chloro styrenes, and vinyl naphthalenes.

The followings are included as examples of the above-mentioned hydroxyl-containing monomers: 2-hydroxyethyl acrylates, 2-hydroxyethyl methacrylates, hydroxypropyl acrylates, hydroxypropyl methacrylates, hydroxybutyl acrylates, hydroxybutyl methacrylates, allyl alcohols, and methallyl alcohols.

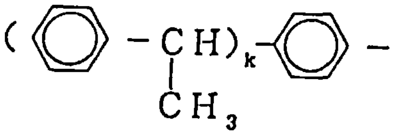
Also, the following monomers which are known as reactive emulsifiers may be utilized as the above-mentioned first monomer having a polar group:

ANTOX-MS-60 (product name; manufactured by Nippon Nyukazai Co., Ltd.) represented by the structural formula:

Chemical structural formula 3

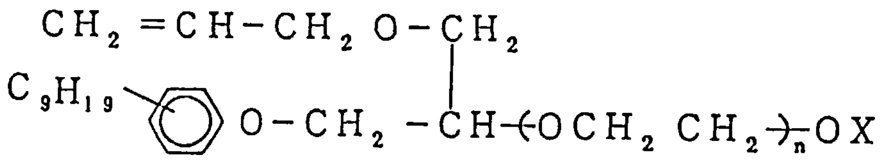


wherein m + n = 20 and R:



ADEKASOAP SE-10N (product name; manufactured by Asahi Denka Kogyo K.K.) represented by the structural formula:

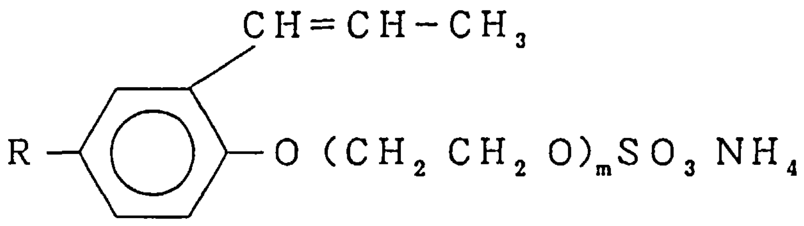
Chemical structural formula 4



wherein X:H or SO_3NH_4

AQUARON HS-10 (product name; manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd.) represented by the structural formula:

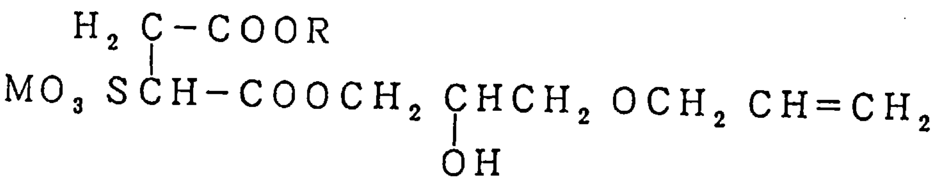
Chemical structural formula 5



wherein R:C_9H_{19} and m = 10

LATEMUL S-180A (product name; manufactured by Kao Corporation) represented by the structural formula:

Chemical structural formula 6

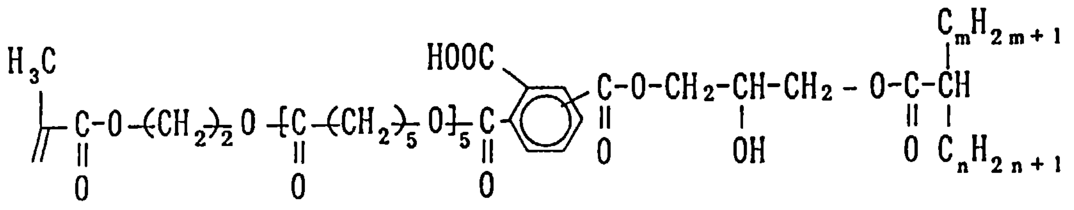


$$\begin{array}{l} \qquad\quad H_2C-COOR \\ \qquad\qquad\ | \\ MO_3SCH-COOCH_2CHCH_2OCH_2CH=CH_2 \\ \qquad\qquad\qquad\qquad\qquad\ | \\ \qquad\qquad\qquad\qquad\qquad OH \end{array}$$

wherein R:$C_{18}H_{36}F_1$ and M:NH_4

A reactive emulsifying agent having a terminal hydroxyl group which is represented by the structural formula:

Chemical structural formula 7



wherein m + n = 9

The above compound as reperesented by the structural formula 7 is obtainable by reacting with trimellitic anhydride, a compound which is prepared by adding 5 moles (on average) of ε-caprolactone to one mole of 2-hydroxyethyl methacrylate to allow the trimellitic anhydride to undergo a ring-opening reaction, and thereafter reacting one of carboxyl groups resulted from the ring-opening with a long-chain epoxy (KARJULAR E).

Another applicable compound is obtainable by reacting phthalic anhydride with 2-hydroxyethyl methacrylate to allow the former to undergo a ring-opening reaction. Exemplary of such a compound is ACRYLESTER PA (name used in trade and manufactured by Mitsubishi Rayon Co., Ltd.).

A proportion of the first monomer having a polar group to be copolymerized depends upon the type and the other characteristics of the second monomer to be copolymerized therewith. The proportion may be determined such that the swelling degree of the resulting copolymer falls within the above-stated range.

Preferred structures of a non-polar site located in the charge-imparting polymer include alkyl chains having 4 or more carbon atoms, polydimethyl siloxane chains, and fluorocarbon chains.

[Molecular Weight]

A number average molecular weight of the charge-imparting polymer employed for the present invention preferably ranges from 3,000 to 20,000, more preferably from 5,000 to 15,000. This number average molecular weight is a polystyrene equivalent average molecular weight as determined by GPC (Gel Permeation Chromatography). In general, as the number average molecular weight of the charge-imparting polymer falls below the above-specified range, the charge-imparting polymer shows a trend of increasing dissolution in the non-aqueous medium to render the above-described swelling degree thereof unmeasurable. The use of a liquid developer containing such a charge-imparting polymer more likely results in reduced image densities. On the other hand, as the number average molecular weight of the charge-imparting polymer goes beyond the above-specified range, an increasing degree of flocculation of toner particles is caused to allow the size thereof in diameter to increase. This also results in a broad distribution of toner particle sizes.

[Loadings of the charge-imparting polymer]

In accordance with the present invention, the amount of the charge-imparting polymer to be incorporated in the liquid developer may be suitably determined depending upon the particular types, amounts and particle sizes of the toner particles employed. The charge-imparting polymer is added in the amount of preferably from 0.5 % to 20 % by weight, more preferably from 1 % to 5 % by weight, based on the solids content of the toner particles. Incorporation of the charge-imparting polymer in an exceedingly reduced amount possibly results in its failure to impart an adequate amount of charge to the toner particles. This may cause the density of the resulting images to be lowered. On the other hand, the addition of an excessively large amount of the charge-imparting polymer tends to promote flocculation of the toner particles.

Toner Particles

The type of the toner particles applicable to the present invention is not particularly limited, and any resin particles which are found to be useful for the liquid developer may be employed. Such toner particles may be prepared so as to contain a colorant therein. Alternatively, the toner particles and the colorant may be separately added to a medium to form an admixture.

The colorant may be suitably incorporated into the toner particles through such techniques as wet milling, latex mixing, and interfacial polymerization. Those techniques for preparing such toner particles are described below.

The wet milling involves adding a colorant to a melted resin to form a mixture. The mixture is transferred into a solvent which is subsequently milled under a proper temperature condition, accompanied by the presence of protective colloids when needed, such as by a ball milling apparatus to form the toner particles containing the colorant therein.

The latex mixing involves adding a colorant to latex particles prepared through dispersion polymerization in a non-aqueous medium, followed by mixing thereof such as by the ball milling apparatus to result in toner particles containing the colorant therein.

The interfacial polymerization method utilizes an interfacial polymerization reaction to encapsulate colorant such as pigment and/or dye within a resin, thereby forming resin-encapsulated particles as the toner particles containing the colorant therein. The resin material for forming a shell wall of the microcapsules prepared through the interfacial polymerization must be soluble in a non-aqueous medium. Examples of suitable resins include polyurethane resins and polyurea resins. The resin can be prepared through the interfacial polymerization, for example, by reacting a first compound, as a first resin precursor, having two or more amino and/or hydroxyl groups with a second compound, as a second resin precursor, having two or more isocyanate groups. More specifically, the colorant to be embedded within the microcapsule is dispersed or dissolved in one of the first and second compounds, whichever insoluble to the non-aqueous medium, optionally in the presence of a dispersion stabilizer. Subsequently, a non-aqueous dispersion medium is added to the dispersion or solution to allow the same to be dispersed therein to form a emulsion, if necessary, in the presence of a protective colloid, followed by adding thereto the other of the first and second compounds for interfacial polymerization.

The size of the toner particles suitable for employment in the present invention ranges preferably from 0.05 to 5μm in diameter, more preferably from 0.2 to 2μm. If the size becomes excessively small, fogging is more likely to be generated in the resulting images. On the other hand, if the size becomes excessively large, a reduced resolution possibly results.

The amount of the toner particles contained in the liquid developer of the present invention is not particularly specified, and can be chosen from those conventionally employed for liquid developers. For example, the amount ranges preferably from 0.5 to 50 weight %, more preferably from 1 to 3 weight %, based on a total amount of the liquid developer. If the toner particles content is exceedingly low, clear images may not result, while if it goes excessively high, an increased degree of flocculation of the toner particles possibly result.

The toner particles for use in the present invention are contemplated to receive an electrical charge from the charge-imparting polymer. However, this is not intended to exclude those toner particles into which a polar group has been introduced. For example, a resin having an acid or polar group, such as an ethylene/methacrylic acid copolymer or a vinyl acetate/methacrylic acid copolymer, may be utilized as a main component of the toner particles. Alternatively, a protective collid having a acid or basic group may be utilized for adsorption thereof to resin particles.

Non-aqueous Medium

Any non-aqueous medium which is applicable to the dispersion medium for the liquid developer can be employed for the present invention. Typically, such non-aqueous medium has a volume resistivity of at least 10^9 Ωcm, and a dielectric constant of at least 3.5. Examples of suitable non-aqueous medium include aliphatic hydrocarbons, alicyclic hydrocarbons, aromatic hydrocarbons, halogenated hydrocarbons, and polysiloxanes. An isoparaffin petroleum solvent is advantageous when empolyed to avoid volatility, safety, toxicity, and odor concerns. Such isoparaffin petroleum solvents include ISOPAR M, ISOPAR G, ISOPAR H, ISOPAR L, ISOPAR K (names used in trade and manufactured by Esso Sekiyu K.K.), and SHELLSOL 71 (name used in trade and manufactured by Shell Sekiyu K.K.).

Colorant

The colorant for use in the present invention can be selected from a wide variety of colorants which are applicable to the liquid developers. Known colorants include inorganic pigments, organic pigments, dyes, and any mixtures thereof.

The follwings are specific examples of the pigments:

Magenda pigments: azolakes, monoazolakes, and quinacridones etc., ... C.I. Pigment Nos. Red-57-1, Red-31, Red-122, Red-48:3, and Red-48:4 etc.;
Cyan pigments: phthalocyanines etc., ... C.I. Pigment Nos. Blue-60, Blue-15-6, Blue-15, Blue-15-2, Blue 15-3, and Blue-15-4 etc.;
Yellow pigments: diazo and benzoimidazolines etc., ... C.I. Pigment Nos. Yellow-12, -13, 14, -17, -55, -83, and - 154 etc.; and
Black pigments: carbon black, copper oxides, manganese dioxides, aniline black, activated carbon, magnetites, magnetic ferrites, and non-magnetic ferrites etc..

The followings are specific examples of the dyes:

C.I. Direct Black 19, 22, 154;
C.I. Direct Yellow 12, 16, 88;
C.I. Direct Red 9, 13, 17;
C.I. Direct Blue 78, 90;
C.I. Acid Black 8, 31, 52;
C.I. Acid Yellow 23, 25;
C.I. Acid Red 37, 52, 92, 94;
C.I. Acid Blue 9, 22; and
C.I. Food Black 2.

The colorant content is not particularly limited but is preferably 5-40 weight %, based on a total amount of the colorant and a resin component of the toner particles. An excessively reduced colorant content results in failure to provide clear images, whereas an excessively high colorant content results in poor charge stability of the liquid developer.

The liquid developer of the present invention is capable of imparting an adequate amount of charge to the toner particles without a charge director commonly used in the art. However, such addition is not intended to be exclusive, and if desired, the charge director can be added to the liquid developer. The followings are examples of applicable charge directors.

The charge directors imparting a positive charge include dioctyl sodium sulfosuccinates, zirconium octoates, copper oleates, metal salts of naphthenic acid, metallic complex salts of ethylenediaminetetraacetic acid, quaternary ammonium compounds and the like.

The charge directors imparting a negative charge include lecithin, barium petronates, alkylsuccineimides, oil black BY and the like.

One exemplary procedure for preparing the liquid developer of the present invention is described below.

Firstly, a non-aqueous medium is prepared which contains toner particles in their dispersed form. The non-aqueous medium is then combined with another medium having a polarity higher that that of the non-aqueous medium to form a combined medium. The charge-imparting polymer is dissolved in the combined medium, followed by removal of the medium having a polarity higher than that of the non-aqueous medium so that the charge-imparting polymer deposits in its swollen form around the toner particles in the non-aqueous medium.

The above-described medium having a polarity higher than that of the non-aqueous medium is capable of dissolving the charge-imparting polymer therein and preferably has a boiling point lower than that of the non-aqueous medium. The type of the medium having a polarity higher than that of the non-aqueous medium depends upon a particular composition and molecular weight of the charge-imparting polymer employed. Illustrative examples of the medium include methyl isobutyl ketone, methyl ethyl ketone, acetone, normal-butanol, isobutanol, isopropyl alcohol, ethanol, xylene, and toluene. Those polar media are also useful as a solvent for dissolving the charge-imparting polymer, when measuring the aforementioned swelling degree of the charge-imparting polymer.

Since the charge-imparting polymer for employment in the present invention is contraty to the conventional charge directors and high-molecular surface active agents which are fully soluble in the non-aqueous medium, the excess addition of the charge-imparting polymer does not cause a marked increase in volume resistivity of the liquid developer. Also, the charge-imparting polymer is present in the vicinity of the toner particle surface and in a swollen state relative to the non-aqueous medium. This advantageously results in a uniform dispersion of the toner particles and enables the charge-imparting polymer to impart a relatively high amount of charge to the toner particles. All those advantageous features contribute to no generation of fogging, high density and resolution in the resulting images.

The liquid developer in accordance with the present invention has the ability to increase the charge amount of the toner particles while avoiding its marked reduction in volume resistivity, whereby a high density and an excellent resolution of the resulting images can be attained.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The specific embodiments are given below for the purpose of describing the present invention in more detail, but are not intended to be limiting thereof. Throughout the following embodiments, all parts are by weight unless otherwise specified.

Exemplary Preparations of the Charge-Imparting Polymer

Preparation Example 1

A reaction vessel was charged with 60 parts of isobutanol and was maintained at a temperature of 75 °C. A mixture of 50 parts of cetyl methacrylate, 20 parts of polyethylene glycol (15) monomethacrylate (manufatured by Nippon Nyukazai Co., Ltd.; product name: RMA-150M), 30 parts of methacrylic acid, 40 parts of isobutanol, and 2 parts of dimethyl-2,2'-azobis(2-methyl propionate) (manufactured by Wako Pure Chemical Ind., Ltd.; product name: V-601) was dropped over 3 hours, and was further reacted for 5 hours to prepare a copolymer. The copolymer prepared was analyzed by GPC which revealed a number average molecular weight of 12,000.

Also, a swelling degree of the prepared copolymer was measured to be 8.6 g. This measurement was carried out as follows. 1 g of the prepared copolymer was added to 20 g of ISOPAR M. Subsequently, a solvent (isobutanol in this preparation example) used in the polymerization stage was added until the copolymer dissolved therein, followed by removal of the solvent (isobutanol) added using an evaporator to insolubilize the copolymer. After cetrifuging thereof at 3000 G for 30 minutes, a weight of the settled substance was measured. The weight was 9.6 g to result in a swelling degree of 8.6 g.

Preparation Example 2

A reaction vessel was charged with 100 parts of isobutanol and was maintained at a temperature of 85 °C. A mixture of 50 parts of cetyl methacrylate, 15 parts of RMA-150M, 5 parts of hydroxyethyl methacylate, 30 parts of methacrylic acid, 50 parts of isobutanol, and 2 parts of V-601 as a polymerization initiator was dropped over 3 hours, and was further reacted for 5 hours to prepare a copolymer. A mumber average molecular weight and a swelling degree of the copolymer prepared were measured in the same manner as in the above-described Preparation Example 1 to reveal 7,500 and 1.3 g, respectively.

Preparation Example 3

A reaction vessel was charged with 67 parts of methyl ethyl ketone and was maintained at a temperature of 75 °C. A mixture of 30 parts of lauryl methacrylate, 40 parts of styrene, 10 parts of hydroxyethyl methacylate, 20 parts of acrylic acid, and 2 parts of V-601 as a polymerization initiator was dropped over 3 hours, and was further reacted for 5 hours to prepare a copolymer. A mumber average molecular weight and a swelling degree of the copolymer prepared were measured in the same manner as in the above-described Preparation Example 1 to be 14,000 and 3.9 g, respectively.

Preparation Example 4

A reaction vessel was charged with 60 parts of toluen and was maintained at a temperature of 90 °C. A mixture of 80 parts of n-butyl methacrylate, 5 parts of RMA-150M, 5 parts of hydroxyethyl methacylate, 10 parts of ANTOX-MS-NH_4 (name used in trade and manufactured by Nippon Nyukazai Co., Ltd.), 40 parts of toluene, and 2 parts of V-601 as a polymerization initiator was dropped over 3 hours, and was further reacted for 5 hours to prepare a copolymer. A mumber average molecular weight and a swelling degree of the copolymer prepared were measured in the same manner as in the above-described Preparation Example 1 to be 9,000 and 3.0 g, respectively.

Preparation Example 5

A reaction vessel was charged with 60 parts of isobutanol and was maintained at a temperature of 75 °C. A mixture of 45 parts of cetyl methacrylate, 25 parts of RMA-150M, 30 parts of dimethylaminopropyl methacrylamide, 40 parts of isobutanol, and 2 parts of V-601 as a polymerization initiator was dropped over 3 hours, and was further reacted for 5 hours to prepare a copolymer. A mumber average molecular weight and a swelling degree of the copolymer prepared were measured in the same manner as in the above-described Preparation Example 1 to be 11,000 and 5.3 g, respectively.

Preparation Example 6

A reaction vessel was charged with 60 parts of isobutanol and was maintained at a temperature of 75 °C. A mixture of 20 parts of cetyl methacrylate, 50 parts of RMA-150M, 10 parts of hydroxyethyl methacylate, 20 parts of methacrylic acid, 40 parts of isobutanol, and 2 parts of V-601 as a polymerization initiator was dropped over 3 hours, and was further reacted for 5 hours to prepare a copolymer. A mumber average molecular weight of the copolymer prepared was measured in the same manner as in the above-described Preparation Example 1 to be 12,000. The copolymer was observed to fully dissolve in ISOPAR M.

Preparation Example 7

A reaction vessel was charged with 50 parts of toluen and was maintained at a temperature of 100 °C. A mixture of 20 parts of lauryl methacrylate, 60 parts of RMA-150M, 5 parts of hydroxyethyl methacylate, 15 parts of methacrylic acid, 100 parts of toluene, and 3 parts of V-601 as a polymerization initiator was dropped over 3 hours, and was further reacted for 5 hours to prepare a copolymer. A mumber average molecular weight and a swelling degree of the copolymer prepared were measured in the same manner as in the above-described Preparation Example 1 to be 2,000 and 0.2 g, respectively.

Preparation Example 8

A reaction vessel was charged with 60 parts of isobutanol and was maintained at a temperature of 75 °C. A mixture of 35 parts of cetyl methacrylate, 55 parts of RMA-150M, 10 parts of hydroxyethyl methacylate, 40 parts of isobutanol, and 2 parts of V-601 as a polymerization initiator was dropped over 3 hours, and was further reacted for 5 hours to prepare a copolymer. A mumber average molecular weight and a swelling degree of the copolymer prepared were measured in the same manner as in the above-described Preparation Example 1 to be 12,500 and 7.5 g, respectively.

Exemplary Preparation of the Toner Particles

20 parts of phthalocyanine blue (manufactured by Dainichi Seika Colour & Chemicals Mfg. Co., Ltd.; product name: CYANINEBLUE 4966), 80 parts of triethylene glycol, 5 parts of a pigment dispersant (manufactured by ZENEKA Corp.; product name: SOLSPERS 17000), and 125 parts of glass bead (manufactured by Toshiba- ---Corp.; product name: GB 502M) were introduced into a sand grinder, and dispersed at 2000 r.p.m. for 3 hours to prepare a pigment paste.

Meanwhile, 60 parts of cetyl methacrylate, 30 parts of acrylic monomer containing polyalkylene glycol (manufactured by Nippon Nyukazai Co., Ltd.; product name: MA-150), and 10 parts of hydroxyethyl methacrylate were reacted to prepare a copolymer thereof as a protective colloid. 2 parts of the copolymer was dissolved in 150 parts of ISOPAR M to form a solution to which 60 parts of the above-mentioned pigment paste was added. The mixture was subsequently transferred to an emulsifier (MICROFLUIDIZER manufactured by Micro Fluidic Corp.) for emulsification thereof. 0.05 parts of dibutyltin phthalate was then added to the resulting emulsion into which a 30 wt.% ISOPAR M solution in toluendiisocyanate (manufactured by Mitsubishi Kasei Co., Ltd.; product name: TD180) was dropped at room temperature for 1 hour so as to reach an equivalent weight of triethylene glycol as described above. After completion of dropping, the resulting mixture was allowed to remain for 2 hours, and was then heated to a temperature of 45 °C for further polymerization.

Particle sizes of the particles obtained were measured by a particle size measuring equipment (SALAD 200A; manufatured by Shimadzu Corp.) which revealed an average particle size of 0.7 μm.

EXAMPLES

EXAMPLE 1

100 parts (30 weight % solids content) of the toner dispersion obtained in the above exemplary preparation, 2 weight % of the charge-imparting polymer of Preparation Example 1 based on the solids content of the toner dispersion, and a sufficient amount to dissolve the charge-imparting polymer, i.e., 12 parts of isobutanol were mixed with agitation. The mixture was then distilled to remove isobutanol. As a result, a toner dispersion was prepared wherein the charge-imparting polymer deposited in the vicinity of toner particle surface.

Secondly, a cationic polymer consisting of 30 parts of cetyl methacrylate and 70 parts of dimethylaminoethyl methacrylamide and having a number average molecular weight of 17,600 was prepared as a soluble polymer containing a polar group which has a polarity opposite that of a polar group contained in the charge-imparting polymer. Added to the above-prepared toner dispersion was 2 weight % of the cationic polymer based on solids content of the toner dispersion so that a negatively charged liquid developer was obtained.

The resulting liquid developer was diluted with ISOPAR M to a 1.5 % toner concentration, and was thereafter utilized for printing by a printer (SAVIN 9040). An image density in an image area and fogging in a non-image area were respectively measured using a Macbeth densitometer. The densities in the image and non-image areas were 1.60 and 0.03, respectively.

EXAMPLES 2-4

Negatively charged liquid developers were obtained in the same manner as in Example 1 except that the charge-imparting polymer of Example 1 was replaced with respective one of those obtained in the above Preparation Examples 2-4 and the solvents used respectively in Preparation Examples 2-4 were employed as the polar solvents for dissolving the respective charge-imparting polymers. The resulting densities in the image and non-image areas are shown in Table 1.

EXAMPLE 5

A positively charged liquid developer was obtained in the same manner as in Example 1 except that the charge-imparting polymer and the cationic polymer of Example 1 were respectively replaced with the charge-imparting polymer of Preparation Example 5 and zirconium octoate as a charge director.

The liquid developer thus prepared was applied to an electrophotographic, original printing plate of a scanning light exposure type plate setter (manufactured by Printwear Inc., U.S.A.; 1440EZ PLATESETTER) which incorpoates a semiconductor laser with a 780 nm wavelength as a light source to form a plate-set image. Thereafter, a toner-free sensitized layer in the non-image area was dissolved for removal utilizing an alkali liquid developer (manufactured by Printwear Inc., U.S.A.; DEVELOPER FOR 1440EZ), followed by a protective treatment with a liquid gum to prepare a lithographic printing plate which retained images formed by toner as its image area. The printing plate thus obtained was mounted to a compact offset press (manufactured by Hamade Printing Machine Mfg. Co.,Ltd.; HAMADASTAR 7000CDX), followed by printing on a wood free paper using a commercially available ink. Image densities of the resulting print and fogging in a non-image area were measured using the Macbeth densitometer. The measurement results are shown in Table 1.

COMPARATIVE EXAMPLE 1

A negatively charged liquid developer was obtained in the same manner as in Example 1 except that the charge-imparting polymer was not employed. The densities in the image and non-image areas were measured in the same manner as in the above Example 1. The results are shown in Table 1.

COMPARATIVE EXAMPLES 2-4

Negatively charged liquid developers were obtained in the same manner as in Example 1 except that the charge-imparting polymer of Example 1 was replaced with respective one of those obtained in the above Preparation Examples 6-8 and the solvents used respectively in Preparation Examples 6-8 were employed as the polar solvents for dissolving the respective charge-imparting polymers. The densities in the image and non-image areas were measured in the same manner as in the above Example 1. The results are shown in Table 1.

Table 1

		*CIP Prep. Ex. No.	Polar Solvent	Ionic Species of *CIP	Properties of *CIP		Printing Char. (Image Density)	
					$\overline{Mn}$	Deg. of Swelling (g)	Image Area	Non-Image Area
Ex. No.	1	1	ISOBUTANOL	CARBOXYLIC GP.	12,000	8.6	1.60	0.03
	2	2	ISOBUTANOL	CARBOXYLIC GP.	7,500	1.3	1.50	0.02
	3	3	*MEK	CARBOXYLIC GP.	14,000	3.9	1.55	0.03
	4	4	TOLUENE	SULFONIC GP.	9,000	3.0	1.53	0.03
	5	5	ISOBUTANOL	AMINO GP.	11,000	5.3	1.48	0.04
Comp. Ex. No.	1	N/A	---	---	---	---	0.98	0.04
	2	6	ISOBUTANOL	CARBOXYLIC GP.	12,000	Fully Dissolved	0.65	0.18
	3	7	TOLUENE	CARBOXYLIC GP.	2,000	0.2	1.08	0.03
	4	8	ISOBUTANOL	NONION	12,500	7.5	1.05	0.03

* CIP = Charge-Imparting Polymer
MEK = Methyl Ethyl Ketone

As apparent from Table 1, the use of the liquid developer of the present invention results in the reduced fogging in the non-image area and the increased image densities in the image area.

Claims

1. A liquid developer including:

toner particles;
a non-aqueous medium for dispersing said toner particles; and

a charge-imparting polymer present in the vicinity of the toner particle surface, the charge-imparting polymer containing a polar group comprising at least one of acid and basic groups for imparting charges to the toner particles, a swelling degree of the charge-imparting polymer relative to said non-aqueous medium being equal to or greater than 0.5 g.

2. The liquid developer in accordance with claim 1 wherein a number average molecular weight of said charge-imparting polymer ranges from 3,000 to 20,000.

3. The liquid developer in accorance with claim 1 further including a soluble polymer which contains a polar group having a polarity opposite that of said polar group contained in the charge-imparting polymer and is soluble in said non-aqueous medium.

4. The liquid developer in accordance with claim 1 wherein said charge-imparting polymer is contained in said non-aqueous medium by dissolving the charge-imparting polymer in a combined medium of the non-aqueous medium and a medium having a polarity higher than that of the non-aqueous medium, and thereafter removing the medium having a relatively higher polarity in the presence of said toner particles.

5. The liquid developer in accordance with claim 1 wherein said toner particles are colorant-containing resin particles.

6. The liquid developer in accordance with claim 1 wherein said toner particles are resin-encapsulated colorant particles prepared through interfacial polymerization in a non-aqueous medium.

7. The liquid developer in accordance with claim 6 wherein said resin particles are obtainable by dispersing in said non-aqeuous medium a first resin precursor containing said colorant, adding thereto a second resin precursor which is soluble in said non-aqueous medium, and polymerising said first and second resin precursors.

8. A method for preparing the liquid developer of Claim 1 comprising the steps of:

combining a non-aqueous medium containing toner particles in a dispersion form with a medium having a polarity higher than that of the non-aqueous medium to form a combined medium;
dissolving a charge-imparting polymer in said combined medium; and
removing said medium having a relatively higher polarity from the combined medium including the dissolved charge-imparting polymer.

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 10 8054

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP 0 695 974 A (NIPPON PAINT CO LTD) 7 February 1996 * page 6 - page 8; example 1 * ---	1,6	G03G9/12 G03G9/13
X	US H1483 H (LARSON JAMES R ET AL) 5 September 1995 * example XII * * the whole document * ---	1	
X	US 5 409 796 A (FULLER TIMOTHY J ET AL) 25 April 1995 * example XIV * * the whole document * ---	1	
X	DE 23 38 249 A (RICOH KK) 21 February 1974 * examples * ---	1	
X	GB 1 382 260 A (RICOH KK) 29 January 1975 * example 1 * ---	1	
X	FR 2 196 489 A (CANON KK) 15 March 1974 * example 1 * -----	1	TECHNICAL FIELDS SEARCHED (Int.Cl.6) G03G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	29 July 1997	Heywood, C

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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