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(54) Toner for developing electrostatic images and a method of manufacturing the same.

(57) A toner for developing electrostatic images, comprises spheroidal resin particles having a binding resin as the main component, with the particles being prepared by dispersion polymerization and colored by a disperse dye, and the volume-average particle size of the particles being within the range of 4 to 8 µm, the content of particles of 4 µm or smaller size being 10 weight percent or less.

TONER FOR DEVELOPING ELECTROSTATIC IMAGES AND A METHOD OF MANUFACTURING THE SAME

The present invention relates to toner for developing electrostatic images used in electrophotography or the like, to a method of manufacturing the same, more particularly to colored toner having good image resolution and fixing characteristics and easy to manufacture, and to a method of manufacturing the same.

Generally, the toner used in the field of electrophotography or the like for developing electrostatic images is formed from colored resins of 5 to 20 µm size that consist of colorants, charge control agents, etc. dispersed in a resin medium. With the recent rise in demand for high-quality image production on image forming apparatus used in electrophotography or the like, there has arisen a need for toner having a small particle size and a limited particle size distribution, in order to achieve production of high-quality, high-resolution images. The resin medium used includes a resin, such as styrene base resins, that have desired electrostatic and binding properties, while the colorants used include carbon black and other organic or inorganic color pigments. The charge control agents used include nigrosine, monoazo dyes, or metallic complexes of salicylic acid or naphthoic acid, etc. Such toner for developing electrostatic images has previously been manufactured by a method in which the resin medium, colorants, and charge control agents are melted and kneaded and the thus kneaded mixture is crushed and classified. However, this method of manu facturing toner by crushing and classifying has had the problem that the yield of toner is extremely low, wasting expensive materials such as colorants and, requiring high equipment cost, hence the difficulty in reducing the product cost.

In view of the above problems, there has been proposed a method (as disclosed in Japanese Laid-open Patent Publication No. 63-106667) wherein resin particles, the size of which has been selected through classification, are dispersed in an aqueous medium and are then colored using a disperse dye. According to this method, colored resin particles can be easily obtained, and by changing the kinds of dyes, toners of various colors can be produced. However, this method also involves a complicated manufacturing process because of the need for classification. Furthermore, in this method it is difficult to obtain particles having a sufficiently small range of particle size distribution even through classification. It is particularly difficult to obtain small-size, monodisperse particles suitable for high-quality image production.

On the other hand, it is known that small-size, monodisperse particles can be produced by dispersion polymerization wherein polymerization is performed in a medium comprising a mixture of water and a water-miscible organic solvent in the presence of a dispersion stabilizer. Japanese Laid-open Patent Publication No. 61-228458 discloses a method of manufacturing toner whereby resin particles produced by dispersion polymerization are colored using an oil-soluble dye. According to this method, toner having particle size distri bution suitable for high-quality image production can be obtained. However, in this method, since colored polymer particles become fused to each other when conventional filter equipment is used during the process of separating them from the aqueous medium, freeze-drying must be performed, thus complicating the manufacturing process.

The toner for developing electrostatic images of the present invention, comprises spheroidal resin particles having a binding resin as its main component, wherein the particles are prepared by dispersion polymerization and colored by a disperse dye and the volume-average particle size of the particles is within the range of 4 to 8 µm, the content of particles of 4 µm or smaller size being 10 weight percent or less.

In a preferred embodiment, the volume-average particle size of the particles is within the range of 5 to 8 µm.

In another preferred embodiment, the content of the particles of 4 µm or smaller size is within the range of 0 to 5 weight percent.

In still another preferred embodiment, the binding resin contains as constituent(s) thereof acrylic acid ester and/or methacrylic acid ester to 30 to 90 weight percent.

A method of manufacturing toner for developing electrostatic images according to this invention comprises the steps of obtaining spheroidal resin particles by dispersion polymerization of a monomer forming a binding resin in a solution containing water and a water-miscible organic solvent in the presence of a dispersion stabilizer; and dyeing the resin particles with a disperse dye by dispersing the resin particles and the disperse dye in an aqueous medium and heating the mixture to a temperature within the range from the glass-transition point of the resin to a temperature 40°C above the glass-transition point thereof.

Preferably the temperature at which the resin particles are dyed by the disperse dye is within the range from the glass-transition point of the resin to a temperature 30°C above the glass-transition temperature thereof.

Thus, the invention described herein makes possible one or more of the objectives of (1) providing coloured toner for developing electrostatic images which has a small particle size and a monodisperse particle size distribution; (2) providing toner for developing electrostatic images which has good image resolution, such as fine line reproducibility, and fixing characteristics; (3) providing toner for developing electrostatic images which does not cause fogging and splashing of toner; (4) providing toner for developing electrostatic images suitable for a high-quality image forming apparatus; and (5) providing a method of manufacturing toner for developing electrostatic images having the above-mentioned excellent characteristics.

The binding resin used for the present invention has a hydrophobic polymer as its main component. Monomers used for forming this polymer include hydrophobic monomers such as vinyl aromatic monomers, acrylic monomers, vinyl ester monomers, vinyl ether monomer, and olefinic monomers. The vinyl aromatic monomers include, for example, styrene, α-methylstyrene, vinyltoluene, α-chlorostyrene, o-,m-,p-chlorostyrene, p-ethylstyrene, and divinylbenzene. Acrylic acid or methacrylic acid ester (hereinafter collectively referred to as (meth)acrylic acid ester) is used as the acrylic monomers, which include, for example, methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, cyclohexyl acrylate, phenyl acrylate, methyl methacrylate, hexyl methacrylate, 2-ethylhexyl methacrylate, β-hydroxyethyl acrylate, γ-hydroxypropyl acrylate, δ-hydroxybutyl acrylate, β-hydroxyethyl methacrylate, and ethyleneglycol dimethacrylate. The vinyl ester monomers include, for example, vinyl formate, vinyl acetate, and vinyl propionate. The vinyl ether monomers include, for example, vinyl-n-butyl ether, vinyl phenyl ether, and vinyl cyclohexyl ether. The olefinic monomers include, for example, ethylene, propylene, isobutylene, butene-1, pentene-1, and 4-methylpentene-1. One of these monomers or a combination of two or more of them are used. In particular, when (meth)acrylic acid ester is used in combination with other monomers, the dye affinity of the resin is enhanced. It is desirable that the amount of (meth)acrylic acid ester used be adjusted so that the copolymer resulting from the polymerization contains the (meth)acrylic acid ester component of 30 to 90 weight percent.

The disperse dyes used for the present invention include such water-insoluble dyes as azo dyes, anthraquinone dyes, indigoid dyes, sulphur dyes, and phthalocyanine dyes. It is desirable that the dyes have a high affinity for the binding resin used and be capable of firmly dyeing the resin particles. Accordingly, optimum dyes are selected according to the chemical composition of the resin. Furthermore, it is desirable that the dyes be formed from fine powder having a particle size smaller than 5 µm, and preferably smaller than 2 µm. Such fine powder can be produced, for example, by using a ball mill or a sand mill.

According to the method of the present invention, the toner for developing electrostatic images is manufactured in the following manner. First, the above monomers are dispersed for polymerization in a solution containing water and a water-miscible organic solvent in the presence of a dispersion stabilizer.

The water-miscible organic solvents which can be used include, for example, lower alcohols such as methanol, ethanol, isopropanol, etc.; ketones such as acetone, methyl ethyl ketone, methyl butyl ketone, etc.; ethers such as tetrahydrofuran, dioxane, etc.; esters such as ethyl acetate, etc.; and amides such as dimethylformamide, etc. The organic solvent is selected suitably in accordance with the kind of monomer used.

The mixing ratio of the water to the water-miscible organic solvent depends on the kind of the monomer and the kind of the organic solvent used, the ratio being so determined that the monomer can be dissolved uniformly in the solution. Generally, the ratio should be within the range of 40:60 to 5:95 by weight, and preferably within the range of 30:70 to 10:90 by weight. For every 100 parts by weight of the monomer, 50 to 5000 parts by weight, preferably 500 to 2500 parts by weight, of the solution is used.

Polymeric dispersion stabilizers soluble in the above solution are desirable for use as the dispersion stabilizer, and include, for example, polyacrylic acid, salts of polyacrylic acid, polymethacrylic acid, salts of polymethacrylic acid, (meth)acrylic acid-(meth)acrylic acid ester copolymer, acrylic acid-vinylether copolymer, methacrylic acid-stylene copolymer, carboxylmethyl cellulose, polyethylene oxide, polyacrylamide, methyl cellulose, ethyl cellulose, hydroxyethyl cellulose, polyvinyl alcohol, etc. Nonionic or anionic surfactant may also be used. The amount of the dispersion stabilizer added should be 0.1 to 20 weight percent, and preferably 1 to 10 weight percent, with respect to the monomer.

Any known, a polymerization initiator insoluble in water but compatible with the monomer may be further added. For such initiators, azo compounds such as azobisisobutyronitrile, etc. and peroxides such as cumene hydroperoxide, di-t-butylperoxide, benzoyl peroxide, lauroyl peroxide, etc. are used. The mixing ratio of the initiator is not specifically limited, but should generally be 0.1 to 10 weight percent with respect to the monomer. Instead of using such initiators, the polymerization can be initiated by using gamma rays or an accelerated electron beam. Alternatively, the polymerization may be initiated by using photosensitizers in combination with ultraviolet rays.

If desired, charge control agents or other materials may be added to the reactants so that they are contained within the binding resin. The charge control agents used include, for example, nigrosine, monoazo dyes, or metallic complexes such as salicylic acid or naphthoic acid.

A mixture consisting of the monomer, polymerization initiator, solution and, if desired, charge control agent, is slowly stirred for 1 to 50 hours at temperatures of 40 to 90°C to perform polymerization while maintaining the reactants in a uniformly dispersed condition. At this time, the process is preferably conducted in the presence of an inert gas instead of in the presence of oxygen which prevents polymerization. The resulting polymer is filtered, washed by water or other suitable solvent as necessary, and dried to obtain desired resin particles. These resin particles have a volume-average particle size of 4 to 8 μm, and preferably 5 to 8 μm. Furthermore, the resin particles contain particles of 4 μm or smaller size in the proportion of 10 weight percent or less, with respect to the total weight of the entire particles, and preferably does not contain particles smaller than 4 μm.

Next, the thus produced resin particles and the disperse dye are dispersed in an aqueous medium and heated to a temperature within the range from the glass-transition point of the resin to 40°C above the glass-transition point thereof, to dye the resin particles.

Generally water is used as the aqueous medium. However, if there is any difficulty in dispersing the resin particles and the dye, a suitable organic solvent may be added in small quantities. A minimum of 500 parts by weight of aqueous medium is preferably used for every 100 parts by weight of resin particles.

The resin particles and the disperse dye are dispersed in the aqueous medium. It is desirable that a minimum of 2 weight percent, preferably 4 weight percent, of the dye be used with respect to the weight of the resin particles so that the resin particles are provided with enough color density to serve as toner. Charge control agents, fluidizer agents, fillers, etc. may further be added if desired.

The thus prepared dispersion liquid is heated to a temperature within the range from the glass-transition point of the resin to 40°C above the glass-transition point thereof while the liquid is being stirred. If the temperature of the dispersion liquid is lower than the glass-transition point, the resulting resin particles have either difficulty in dyeing the resin particles in the desired color density or need longer time for dyeing. If the temperature of the dispersion liquid is higher than 40°C above the glass-transition point, the resin particles are fused and adhere to each other, forming blocks of particles.

The thus dyed resin particles are filtered and dried to produce the toner for developing electrostatic images according to the present invention.

The toner for developing electrostatic images according to the present invention comprises fine particles with a volume-average particle size of 4 to 8 μm, as described, and provides excellent image resolution, such as fine line reproducibility, and fixing characteristics. Furthermore, the toner for developing electrostatic images according to the present invention contains particles of 4 μm or smaller size in less than 10 weight percent or less with respect to the weight of the entire particles, thus alleviating the trouble of fogging and splashing of toner which tends to occur due to insufficient charging of fine-size particles. Generally, it is required that fine powder toner for high-quality image forming apparatus be dyed in higher density. The toner for developing electrostatic images according to the present invention contains 30 to 90 weight percent of (meth)acrylic acid ester as a constituent of the binding resin and therefore has an excellent dye-affinity, enabling high-density dyeing to be achieved under mild conditions. Therefore, the toner for developing electrostatic images according to the present invention can be used suitably as toner for high-quality image forming apparatus.

According to the method of the present invention, the toner having the above-mentioned excellent characteristics is produced without any difficulty. Furthermore, since crushing and classifying processes are not needed in the method of the present invention, high yield of toner is achieved, and colorants and other materials are not wasted, enabling the toner having the above-mentioned excellent characteristics to be manufactured at low costs. Moreover, since toners of various colors can be obtained by changing the kinds of dyes, it is easy to manufacture various kinds of toners in small quantities.

The present invention will be described with reference to the following non-limiting examples.

Examples 1-3

Using the composition shown in Table 1, polyacrylic acid was dissolved in a medium comprising a mixture of water and isopropyl alcohol, to which styrene , methyl methacrylate, styrene sulfonic acid sodium salt, and azobisisobutyronitrile were added. The thus prepared liquid was placed for reaction in a 500 ml separable flask while the liquid was being stirred in a 50 rpm stream of nitrogen at 70°C for 12 hours, the polymerization being thus completed. The resulting emulsion was filtered, washed, and dried to obtain white-colored polymer particles. Table 2 shows the volume-average particle sizes of three different kinds of particles, each having different content of methyl methacrylate, and the weight percent of particles contained therein having 4 µm or smaller size, as well as the glass-transition points (Tg) and melting points (Tm) thereof. The volume-average particle sizes of all particles fall within the range of 5.8 to 6.5 µm with no particles of 4 µm or smaller size. Also, the values of Tg and Tm are very similar between the three examples.

For the polymer particles of each example, 50 g of polymer particles, 6 g of blue quinone disperse dye (SPR Blue 1, manufactured by Mitsui Toatsu dyes) and an aqueous dispersion stabilizer were dispersed in 500 g of water, which was placed in a 1-liter flask and stirred for 5 hours at 85°C for dyeing the particles. The particles were then filtered, washed and dried to obtain blue-colored particles. The thus dyed particles of each of the three examples were dissolved in tetrahydrofuran, and the content of dye in the polymer particles was calculated by measuring the light absorption using a spectrophotometer. The results are shown in Table 3. In the case of the particles of Example 1 composed of polystyrene of 100% purity, about 20% of the dye added under the above conditions was introduced into the particles. On the other hand, in the case of the particles of Example 3 containing 50% methyl methacrylate, almost all of the dye added was introduced into the particles.

The particles of each of the examples were mixed with ferrite carrier and stirred to produce developer which was subjected to a copying test on a Mita Industrial Co., Ltd. Copier Model DC-1205. With all three types of developer, good blue images were obtained. In particular, with the particles of Example 3, an image having better coloring and higher density was obtained than with the particles of Example 1.

Table 1

	Example 1	Example 2	Example 3
styrene (g)	60	45	30
methyl methacrylate	0	15	30
styrene sulfonic acid sodium salt (g)	0.1	0.1	0.1
isopropyl alcohol (g)	240	200	160
water (g)	0	40	80
azobisiso-butyronitrile	2.5	2.5	2.5
polyacrylic acid	3	3	3

Table 2

	Example 1	Example 2	Example 3
content of methyl methacrylate (%)	0	25	50
volume-average particle size (µm)	6.5	6.0	5.8
wt% of particles having 4 µm or smaller size	0	0	0
Tg	92	91	98
Tm	143	152	154

Table 3

	Example 1	Example 2	Example 3
content of methyl methacrylate (%)	0	25	50
content of dye (%)	1.3	7.8	9.7

Example 4 and Comparative Examples 1-2

Using the composition shown in Table 4, polyacrylic acid was dissolved in a medium comprising a mixture of water and isopropyl alcohol, to which sty rene, methyl acrylate, styrene sulfonic acid sodium salt, and azobisisobutyronitrile were added. The thus prepared liquid was placed for reaction in a 500 ml separable flask while the liquid was being stirred in a 50 rpm stream of nitrogen at 70° C for 12 hours, thus completing the polymerization. The resulting emulsion was filtered or centrifuged, and was then washed and dried to obtain white-colored polymer particles. The volume-average particle sizes of the thus obtained particles were 6.1, 3.1, and 10.6, respectively.

For the polymer particles of each type, 50 g of polymer particles, 6 g of a black azo disperse dye (SPR black #200, manufactured by Mitsui Toatsu dyes) and an aqueous dispersion stabilizer were dispersed in 500 g of water, which was placed in a 1-liter flask and was stirred for 5 hours at 85° C for dyeing the particles. The particles were then filtered, washed and dried to obtain black-colored particles.

The above-mentioned black-colored particles of each type were mixed with ferrite carrier and stirred to produce developer with toner concentration of 2 weight percent, which was then subjected to a copying test on a Mita Industrial Co., Ltd. Copier Model DC-1205. With the particles of Example 4, a clear image free from fogging and having good image density and resolution (7 lines/mm) was obtained. On the other hand, with the particles of Comparative Example 1, there was difficulty in obtaining a clear image because of a marked increase in splashing toner. When the toner concentration was reduced to 1 weight percent, the problem of splashing was eliminated but it was only possible to obtain a low-density image. With the particles of Comparative Example 2, no problem was found with the image density, but the resolution dropped to 4 lines/mm.

Table 4

	Example 4	Comparative Example 1	Comparative Example 2
styrene (g)	30	30	30
methyl acrylate (g)	30	30	30
styrene sulfonic acid sodium salt (g)	0.1	0.1	0.1
isopropyl alcohol (g)	160	155	165
water (g)	80	85	75
azobisiso-butyronitrile (g)	2.5	2.5	2.5
polymethacrylic acid (g)	3	3	3

Table 5

	Example 4	Camparative Example 2	Comparative Example 3
volume-average particle size (μm)	6.1	3.1	10.6
volume-reference 25% particle size (μm)	6.7	3.6	11.5
volume-reference 75% particle size (μm)	5.5	2.6	8.9
resolution	7	-	4

Claims

1. Toner for developing electrostatic images, comprising spheroidal resin particles having a binding resin as the main component;

   wherein the particles are prepared by dispersion polymerization and colored by a disperse dye; and

   the volume-average particle size of the particles is within the range of 4 to 8 μm, the content of particles of 4 μm or smaller size being 10 weight percent or less.

2. Toner for developing electrostatic image according to Claim 1, wherein the volume-average particle size of the particles is within the range of 5 to 8 μm.

3. Toner for developing an electrostatic image according to Claim 1 or 2, wherein the content of particles of 4 μm or smaller size is within the range of 0 to 5 weight percent.

4. Toner for developing an electrostatic image according to any preceding claim.

   wherein the binding resin contains as constituent(s) thereof acrylic acid ester and/or methacrylic acid ester to 30 to 90 weight percent.

5. A method of manufacturing toner for an electrostatic image, comprising the steps of; obtaining spheroidal resin particles by dispersion polymerization of a monomer forming a binding resin in a solution containing water and a water-miscible organic solvent in the presence of a dispersion stabilizer; and

   dyeing the resin particles with a disperse dye by dispersing the resin particles and the disperse dye in an aqueous medium and heating the mixture to a temperature within the range from the glass transition point of the resin 40° C above the glass-transition point thereof.

6. A method of manufacture according to Claim 5, wherein the temperature at which the resin particles are dyed by the disperse dye is within the range from the glass-transition point of the resin to 30° C above the glass -transition temperature thereof.

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EUROPEAN SEARCH REPORT

Application Number

EP 90 31 2952

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.5)
X	GB-A-2 114 310 (KONISHIROKU PHOTO IND. CO. LTD.) * abstract; claims 1-34 *	1-4	G 03 G 9/08 G 03 G 9/09
P,X	PATENT ABSTRACTS OF JAPAN vol. 14, no. 88 (P-1008)(4031) 19 February 1990, & JP-A-1 297657 (MATSUSHITA ELECTRIC INDUSTRIAL CO. LTD.) 30 November 1989, * the whole document *	1-4	
X	EP-A-0 297 839 (BANDO CHEM. IND. LTD.) * abstract; claims 1-12 *	5	
Y	US-A-4 617 249 (C. K. OBER, K. P. LOK) * abstract; claims 1-12 *	5	
D,Y	EP-A-0 227 097 (NAGASE CHEMICALS LTD.) * claims 1-9 & JP-A-63106667 (NAGASE CHEM. LTD) 11 May 1988 *	5	
A	US-A-4 837 101 (R. J. GRUBER ET AL.) * claims 1-17 *	1-4	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

G 03 G

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	08 March 91	BATTISTIG M.L.A.

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
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