

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
24 February 2011 (24.02.2011)

PCT

(10) International Publication Number
WO 2011/021675 A1

(51) International Patent Classification:
G03G 9/087 (2006.01) **G03G 9/08** (2006.01)

KABUSHIKI KAISHA, 30-2, Shimomaruko 3-chome,
Ohta-ku, Tokyo, 1468501 (JP).

(21) International Application Number:
PCT/JP2010/064035

(74) Agents: **OKABE, Yuzuru** et al.; No. 602, Fuji Bldg.,
2-3, Marunouchi 3-chome, Chiyoda-ku, Tokyo, 1000005
(JP).

(22) International Filing Date:
13 August 2010 (13.08.2010)

(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ,
CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO,
DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
HN, HR, HU, ID, IL, IN, IS, KE, KG, KM, KN, KP, KR,
KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME,
MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO,
NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE,
SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT,
TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2009-188365 17 August 2009 (17.08.2009) JP

(71) Applicant (for all designated States except US): **CANON
KABUSHIKI KAISHA** [JP/JP]; 30-2, Shimomaruko 3-
chome, Ohta-ku, Tokyo, 1468501 (JP).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **CHIMOTO, Yuya**
[JP/JP]; c/o CANON KABUSHIKI KAISHA, 30-2, Shi-
momaruko 3-chome, Ohta-ku, Tokyo, 1468501 (JP).
KATO, Masayoshi [JP/JP]; c/o CANON KABUSHIKI
KAISHA, 30-2, Shimomaruko 3-chome, Ohta-ku, Tokyo,
1468501 (JP). **HIGASHI, Ryuji** [JP/JP]; c/o CANON
KABUSHIKI KAISHA, 30-2, Shimomaruko 3-chome,
Ohta-ku, Tokyo, 1468501 (JP). **TOYODA, Takayuki**
[JP/JP]; c/o CANON KABUSHIKI KAISHA, 30-2, Shi-
momaruko 3-chome, Ohta-ku, Tokyo, 1468501 (JP). **NA-
TORI, Ryo** [JP/JP]; c/o CANON KABUSHIKI
KAISHA, 30-2, Shimomaruko 3-chome, Ohta-ku, Tokyo,
1468501 (JP). **SHIBATA, Takaho** [JP/JP]; c/o CANON

(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG,
ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ,
TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK,
EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU,
LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK,
SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: PROCESS FOR PRODUCING TONER

(57) Abstract: Disclosed is a process for producing a toner, having an agglomeration step of agglomerating first resin particles and colorant particles in an aqueous medium to form an agglomerate; a primary fusion step of heating a water base dispersion of the agglomerate at an extrapolated glass transition end temperature of the first resin or more to fuse the agglomerate to obtain a water base dispersion of core particles; a cooling step of the water base dispersion of the core particles to a temperature lower than T_{g1}; an adhering step of mixing at a temperature lower than T_{g1} a water base dispersion of second resin particles with the water base dispersion of the core particles to obtain a water base dispersion of the shell-adherent substance; and a secondary fusion step of heating the water base dispersion of the shell-adherent substance at T_{g2} or more to obtain toner particles.



WO 2011/021675 A1

DESCRIPTION

PROCESS FOR PRODUCING TONER

Technical Field

[0001] This invention relates to a process for producing a toner for developing electrostatic latent images which is used in electrophotography, electrostatic recording and so forth.

Background Art

[0002] In recent years, with changes in service environments, there is year after year an increasing tendency for copying machines, printers and so forth to be come higher in the rate of color-image formation. At the same time, because of need for high image quality of high resolution and high gradation, it has become essential for toners to be made small in particle diameter and sharp in particle size distribution. Under such circumstances, in processes for producing toners, too, a process for producing a variety of toners obtained by wet processing, what is called "chemical toners", attracts notice from conventional pulverization process. In particular, an emulsion agglomeration process attracts notice because toners can easily be made small in particle diameter and their particle shapes are easily controllable. As disclosed in Patent Literatures 1, 2 and 3, the emulsion agglomeration process is a process in which a resin particle dispersion solution prepared by a process such as dispersion or emulsion polymerization of resin materials, a colorant particle dispersion solution prepared by dispersing a colorant in an aqueous medium and optionally any other components are subjected to agglomeration to obtain agglomerated particles, and thereafter fusing the agglomerated particles to obtain a toner for electrophotography.

[0003] Meanwhile, in image formation, with an increasing need

for energy saving, it has come to be attempted to make toners fixing at a lower temperature. For one thing, it is proposed to use a resin with a low softening temperature to more lower the fixing temperature. However, because of such a low softening temperature, blocking may occur which is a phenomenon that toner particles unwantedly come to stick together in a condition where they are left to stand, such as during storage or during transportation. Accordingly, a core-shell structure is proposed in which a low softening point resin is covered with a high softening point resin. Such a core-shell structure is considered to enable production of a toner having achieved both heat-resistant storage stability and low-temperature fixing performance.

[0004]How to set up the core-shell structure may include those disclosed in, e.g., Patent Literatures 4 to 6.

[0005]In Patent Literature 4, a method is disclosed in which, in a process making use of emulsion agglomeration, a shell resin is added immediately after agglomerated particles have been obtained, and then the particles are fused to obtain toner particles. However, an attempt to secure the heat-resistant storage stability may make it necessary for the shell resin to be used in a large quantity in order to cover agglomerated particles having a large surface area, resulting in a poor low-temperature fixing performance in some cases.

[0006]In Patent Literature 5, a method is disclosed in which core particles are fused, washed by filtration and then further re-dispersed, and thereafter shell resin is added thereto. In this method, any unreacted core resin fine particles causative of a lowering of heat-resistant storage stability are removed by the washing by filtration and hence this enables good achievement of both the low-temperature fixing performance and the heat-resistant storage stability. However, this method

requires complicated steps and also may make coarse particles form when re-dispersed.

[0007] In Patent Literature 6, a method is disclosed in which core particles are fused and thereafter, in the state the temperature at the time of fusion is maintained, shell particles are dividedly added a plurality of times. Being dividedly added a plurality of times makes the shell particles well fuse together and also makes them well cover the core particles, and this enables achievement of both the low-temperature fixing performance and the heat-resistant storage stability. However, the shell particles are made to adhere to cores at a temperature not lower than the glass transition points of the core and shell resins, and hence this method has a problem that the shell particles tend to fuse together and the core particles tend to fuse through the shell particles, so that fine particles and coarse particles tend to form. Thus, there has been some room for improvement.

Citation List

Patent Literature

- [0008] PTL 1: Japanese Patent Application Laid-open No. S63-282752
PTL 2: Japanese Patent Application Laid-open No. H06-250439
PTL 3: Japanese Patent Application Laid-open No. 2002-351140
PTL 4: Japanese Patent Application Laid-open No. 2006-276073
PTL 5: Japanese Patent Application Laid-open No. 2007-3840
PTL 6: Japanese Patent No. 4135654

Summary of Invention

Technical Problem

[0009] Taking account of the above circumstances, the present invention provides, in a toner production process

making use of emulsion agglomeration, a process for producing a toner having superior fixing performance and heat-resistant storage stability and also succeeded in having kept some particles from becoming coarse.

Solution to Problem

[0010]The present invention is concerned with a process for producing a toner, the process comprising; an agglomeration step of mixing at least a water base dispersion of first fine resin particles having a first resin and a water base dispersion of fine colorant particles and, where an extrapolated glass transition onset temperature of the first resin is represented by T_{ig1} and an extrapolated glass transition end temperature thereof by T_{eg1} , agglomerating at a temperature lower than T_{ig1} the first fine resin particles and the fine colorant particles in an aqueous medium by using of an agglomerating agent to form an agglomerate to obtain a water base dispersion of the agglomerate; a primary fusion step of heating the water base dispersion of the agglomerate at a temperature not lower than T_{eg1} to fuse the agglomerate to form core particles to obtain a water base dispersion of core particles; a cooling step of cooling the water base dispersion of the core particles to a temperature lower than T_{ig1} to obtain a water base dispersion containing the core particles; an adhering step of mixing, at a temperature lower than T_{ig1} , a water base dispersion of second fine resin particles having a second resin and an agglomerating agent with the water base dispersion containing the core particles to make the second fine resin particles adhere to the core particles to form a shell-adherent substance to obtain a water base dispersion of the shell-adherent substance; and a secondary fusion step of heating the water base dispersion of the shell-adherent substance to a temperature not lower than T_{eg1} to obtain toner

particles; and where an extrapolated glass transition onset temperature of the second resin is represented by T_{ig2} , $T_{ig1} < T_{ig2}$.

Advantageous Effects of Invention

[0011]The present invention, in a toner production process making use of emulsion agglomeration, enables production of a toner having superior fixing performance and heat-resistant storage stability and also succeeded in having kept some particles from becoming coarse.

[0012]Further features of the present invention will become apparent from the following description of exemplary embodiments with reference to the attached drawings.

Description of Embodiments

[0013]Materials used in the process of the present invention are described first.

[0014]<Resin>

The first resin and second resin used in the present invention may include, for example, styrene monomers such as styrene, p-chlorostyrene and α -methylstyrene; acrylic ester monomers such as methyl acrylate, ethyl acrylate, n-propyl acrylate, n-butyl acrylate, lauryl acrylate and 2-ethylhexyl acrylate; methacrylate ester monomers such as methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, lauryl methacrylate and 2-ethylhexyl methacrylate; vinyl nitriles such as acrylonitrile and methacrylonitrile; vinyl ethers such as vinylethylether and vinylisobutylether; and homopolymers or copolymers (i.e., vinyl resins) of vinyl ketones such as vinylmethylketone, vinylethylketone and vinylisopropenylketone. Besides, they may include homopolymers or copolymers (i.e., olefin resins) of olefins such as ethylene, propylene, butadiene and isoprene; non-vinyl condensation resins such as epoxy resin, polyester resin, polyurethane resin, polyamide

resin, cellulose resin and polyether resin; and graft polymers including these non-vinyl condensation resins and vinyl monomers. Any of these resins may be used alone or may be used in combination of two or more types. Of these, polyester resin is particularly preferred as having sharp-melt properties and also having superior strength even with a low molecular weight.

[0015]The first resin may preferably have an extrapolated glass transition onset temperature (Tig1) of from 30°C or more to 60°C or less, and much preferably from 40°C or more to 60°C or less. If it has Tig1 of less than 30°C, the whole toner particles may have a low strength to tend to have a low transfer performance and cause toner transport non-uniformity at the time of image endurance testing. Further, the toner particles may agglomerate one another in a high-temperature and high-humidity environment to tend to cause toner transport non-uniformity. If it has Tig1 of higher than 60°C, an inferior image glossiness may result at the time of low-temperature fixing. Here, the above extrapolated glass transition onset temperature and the following extrapolated glass transition end temperature are the values of physical properties that are measured according to JIS (Japanese Industrial Standards) K7121.

[0016]The first resin may preferably have an extrapolated glass transition end temperature (Teg1) having a difference in temperature from Tig1 in that Teg1 is higher than Tig1 within the range of 10°C or less. As a specific temperature range, it may preferably have Teg1 of from 35°C or more to 65°C or less, and much preferably from 45°C or more to 65°C or less. Inasmuch as it is within this range, the toner can maintain a good transfer performance during many-sheet image formation and even after it has been left to stand in a high-temperature and high-humidity environment, and any

toner transport non-uniformity can be kept from coming about. Further, the image glossiness can be more improved.

[0017]The first resin may preferably have a softening temperature (T_{m1}) of from 70°C or more to 110°C or less, much preferably from 70°C or more to 100°C or less, and most preferably from 80°C or more to 100°C or less. Inasmuch as it has T_{m1} within this range, the toner can well achieve both blocking resistance and low-temperature fixing performance, and, where it is incorporated with a wax, can have a good offset resistance. Further, even at a high temperature, any toner melt component is appropriately kept from soaking into paper at the time of fixing, so that images with superior surface smoothness can be obtained. Here, the softening temperature (T_m) is measured with a flow tester (CFT-500D, Shimadzu Corporation). Stated specifically, 1.2 g of a sample to be measured is weighed out, and its softening temperature is measured using a die of 1.0 mm in height and 1.0 mm in diameter and under conditions of a heating rate of 4.0°C/min, a preheating time of 300 seconds, a load of 5 kg and a measurement temperature range of from 40°C or more to 200°C or less. The temperature at which the above sample has flowed out by half is taken as the softening temperature.

[0018]The second resin may preferably have an extrapolated glass transition onset temperature (T_{ig2}) of from 60°C or more to 80°C or less, and much preferably from 65°C or more to 80°C or less. As long as it has T_{ig2} within this range, the toner can well achieve both low-temperature fixing performance and heat-resistant storage stability.

[0019]The relationship between the extrapolated glass transition onset temperature (T_{ig1}) of the first resin and the extrapolated glass transition onset temperature

(Tig2) of the second resin is $Tig1 < Tig2$. Where Tig1 and Tig2 satisfy this relationship, the enclosure of cores by shells is well maintained also at the time of fusion. Their relationship may preferably be $Tig1 + 5^{\circ}C < Tig2$.

[0020]The second resin may preferably be in a proportion to the first resin, of from 5% by mass or more to 30% by mass or less, much preferably from 5% by mass or more to 25% by mass or less, and most preferably from 10% by mass or more to 20% by mass or less. Inasmuch as the proportion of the second resin to the first resin is within this range, core components can appropriately be kept from moving to toner particle surfaces, and hence the toner can have a better heat-resistant storage stability.

[0021]<Colorant>

The colorant used in the present invention may include known organic pigments, dyes, carbon black and magnetic materials.

[0022]As examples of cyan group colorants, included therein are copper phthalocyanine compounds and derivatives thereof, anthraquinone compounds, basic-dye lake compounds and so forth. Stated specifically, they may include C.I. Pigment Blue 1, C.I. Pigment Blue 7, C.I. Pigment Blue 15, C.I. Pigment Blue 15:1, C.I. Pigment Blue 15:2, C.I. Pigment Blue 15:3, C.I. Pigment Blue 15:4, C.I. Pigment Blue 60, C.I. Pigment Blue 62 and C.I. Pigment Blue 66.

[0023]As examples of magenta group colorants, included therein are condensation azo compounds, diketopyrrolopyrrole compounds, anthraquinone compounds, quinacridone compounds, basic-dye lake compounds, naphthol compounds, benzimidazolone compounds, thioindigo compounds, perylene compounds and so forth. Stated specifically, they may include C.I. Pigment Red 2, C.I. Pigment Red 3, C.I. Pigment Red 5, C.I. Pigment

Red 6, C.I. Pigment Red 7, C.I. Pigment Violet 19, C.I. Pigment Red 23, C.I. Pigment Red 48:2, C.I. Pigment Red 48:3, C.I. Pigment Red 48:4, C.I. Pigment Red 57:1, C.I. Pigment Red 81:1, C.I. Pigment Red 122, C.I. Pigment Red 144, C.I. Pigment Red 146, C.I. Pigment Red 166, C.I. Pigment Red 169, C.I. Pigment Red 177, C.I. Pigment Red 184, C.I. Pigment Red 185, C.I. Pigment Red 202, C.I. Pigment Red 206, C.I. Pigment Red 220, C.I. Pigment Red 221 and C.I. Pigment Red 254.

[0024]As examples of yellow group colorants, included therein are compounds as typified by condensation azo compounds, isoindolinone compounds, anthraquinone compounds, azo metal complexes, methine compounds and allylamide compounds. Stated specifically, they may include C.I. Pigment Yellow 12, C.I. Pigment Yellow 13, C.I. Pigment Yellow 14, C.I. Pigment Yellow 15, C.I. Pigment Yellow 17, C.I. Pigment Yellow 62, C.I. Pigment Yellow 74, C.I. Pigment Yellow 83, C.I. Pigment Yellow 93, C.I. Pigment Yellow 94, C.I. Pigment Yellow 95, C.I. Pigment Yellow 97, C.I. Pigment Yellow 109, C.I. Pigment Yellow 110, C.I. Pigment Yellow 111, C.I. Pigment Yellow 120, C.I. Pigment Yellow 127, C.I. Pigment Yellow 128, C.I. Pigment Yellow 129, C.I. Pigment Yellow 147, C.I. Pigment Yellow 151, C.I. Pigment Yellow 154, C.I. Pigment Yellow 155, C.I. Pigment Yellow 168, C.I. Pigment Yellow 174, C.I. Pigment Yellow 175, C.I. Pigment Yellow 176, C.I. Pigment Yellow 180, C.I. Pigment Yellow 181, C.I. Pigment Yellow 191 and C.I. Pigment Yellow 194.

[0025]As black group colorants, they may include carbon black, magnetic materials, and colorants toned in black by using the yellow group colorants, magenta group colorants and cyan group colorants shown above.

[0026]Any of these colorants may be used alone, in the form of a mixture, or in the state of a solid solution. The colorant used in the present invention is selected

taking account of hue angle, chroma, brightness, weatherability, OHP transparency and dispersibility in toner.

[0027] Any of the yellow group colorants, magenta group colorants, cyan group colorants and black group colorants in the present invention may preferably be contained in an amount of from 1 part or more by weight to 20 parts or less by weight based on 100 parts by weight of the terminal resin. If it is in an amount of less than 1 part by weight, the color may insufficiently come out. If it is in an amount of more than 20 parts by weight, any colorant that comes not enclosed in toner particles tends to be larger in amount.

[0028] The water base dispersions of fine resin particles and the water base dispersion of fine colorant particles are described next.

[0029] <Water Base Dispersions of Fine Resin Particles>

The water base dispersion of first fine resin particles and the water base dispersion of second fine colorant particles as used in the present invention are prepared by a known dispersion method. Stated specifically, e.g., an aqueous medium, an emulsifying agent and so forth may be added to the resin, and emulsification making use of external shear force which effects dispersion by means of an apparatus applying a high-speed shear force, such as CLEAMIX (M_{TECHNIQUE} Co., Ltd.), a homomixer or a homogenizer, may be carried out to prepare a resin particle dispersion in water. A resin particle dispersion may also be prepared by a transition phase emulsification process, in which the resin is dissolved in a solvent and this is dispersed in an aqueous medium in the form of particles together with an emulsifying agent, a polymeric electrolyte and so forth by means of a dispersion machine such as a homogenizer, followed by heating or reduced-pressuring

to remove the solvent. Instead, in the case of a resin particle dispersion containing resin particles having a vinyl monomer as a constituent, the resin particle dispersion may also be prepared by emulsification polymerization carried out using an emulsifying agent.

[0030]The first fine resin particles used in the present invention may preferably be non-spherical particles. Stated specifically, the first fine resin particles may preferably be those in which non-spherical particles having a length/breadth ratio in the range of from 1.5 or more to 10 or less are in a number proportion of 95% by number or more of the whole particles and also have an average breadth of from 0.02 μm or more to 1.00 μm or less. Within these ranges so far, the fine resin particles can readily incorporate other toner components such as fine colorant particles and fine release agent particles when the toner is produced, and can well keep components from coming liberated from these particles or coming localized to particle surfaces.

[0031]The first fine resin particles may preferably have a volume base median diameter of from 0.05 μm or more to 1.0 μm or less, and much preferably from 0.05 μm or more to 0.4 μm or less. If the first fine resin particles have a volume base median diameter of more than 1.0 μm , it is difficult to obtain toner particles of from 4.0 μm or more to 7.0 μm or less in diameter, which is weight average particle diameter appropriate for toner particles.

[0032]The second fine resin particles may preferably have a volume base median diameter of from 0.05 μm or more to 0.3 μm or less, and much preferably from 0.08 μm or more to 0.2 μm or less. Having volume base median diameter within this range is preferable in view of readiness to form shells and thickness of the shells formed.

[0033]<Water Base Dispersion of Fine Colorant Particles>

The water base dispersion of fine colorant particles is prepared by dispersing fine colorant particles in an aqueous medium. The fine colorant particles may be dispersed by a known method. For example, a rotary shearing homogenizer, a ball mill, a sand mill, media dispersion machines such as an attritor, high-pressure impact dispersion machines or the like may preferably be used. What may particularly preferably be used are a high-pressure impact dispersion machine (Nanomizer, Yoshida Kikai Co., Ltd.), (Ultimizer, Sugino Machine Limited) and (Nanogesizer LPN series, AC Serendip).

[0034]<Emulsifying Agent>

As the emulsifying agent usable when the water base dispersions are prepared, there are no particular limitations thereon. It may include, e.g., anionic surface active agents of a sulfate ester acid type, a sulfonate type, a phosphate ester type, a soap type and so forth; cationic surface active agents of an amine salt type, a quaternary ammonium salt type and so forth; and nonionic surface active agents of a polyethylene glycol type, an alkylphenol ethylene oxide adduct type and a polyhydric alcohol type. Such an emulsifying agent may be used alone or may be used in combination of two or more types.

[0035]The anionic surface active agents may include, as specific examples thereof, fatty acid soaps such as potassium laurate, sodium oleate, and sodium castor oil; sulfate esters such as octyl sulfate, lauryl sulfate, lauryl ether sulfate, and nonyl phenyl ether sulfate; alkyl naphthalene sulfonates such as lauryl sulfonate, dodecylbenzene sulfonate, triisopropyl naphthalene sulfonate, and dibutyl naphthalene sulfonate; sulfonates such as naphthalene sulfonate formalin condensation product,

mono-octyl sulfosuccinate, dioctyl sulfosuccinate, lauric acid amide sulfonate, and oleic acid amide sulfonate; phosphate esters such as lauryl phosphate, isopropyl phosphate, and nonyl phenyl ether phosphate; dialkyl sulfosuccinates such as sodium dioctyl sulfosuccinate; and sulfosuccinates such as disodium lauryl sulfosuccinate.

[0036] The cationic surface active agents may include, as specific examples thereof, amine salts such as laurylamine hydrochloride, stearylamine hydrochloride, oleylamine acetate, stearylamine acetate, and stearyl aminopropylamine acetate; and quaternary ammonium salts such as lauryl trimethyl ammonium chloride, dilauryl dimethyl ammonium chloride, stearyl trimethyl ammonium chloride, distearyl dimethyl ammonium chloride, lauryl dihydroxyethyl methyl ammonium chloride, oleyl bispolyoxyethylene methyl ammonium chloride, lauroyl aminopropyl dimethyl ethyl ammonium ethosulfate, lauroyl aminopropyl dimethyl hydroxyethyl ammonium perchlorate, alkylbenzene trimethyl ammonium chloride, and alkyl trimethyl ammonium chloride.

[0037] The nonionic surface active agents may include, as specific examples thereof, alkyl ethers such as polyoxyethylene octyl ether, polyoxyethylene lauryl ether, polyoxyethylene stearyl ether, and polyoxyethylene oleyl ether; alkyl phenyl ethers such as polyoxyethylene octyl phenyl ether, and polyoxyethylene nonyl phenyl ether; alkyl esters such as polyoxyethylene laurate, polyoxyethylene stearate, and polyoxyethylene oleate; alkyl amines such as polyoxyethylene lauryl amino ether, polyoxyethylene stearyl amino ether, polyoxyethylene oleyl amino ether, polyoxyethylene soybean amino ether, and polyoxyethylene beef tallow amino ether; alkyl amides such as polyoxyethylene lauric acid amide, polyoxyethylene stearic acid amide, and polyoxyethylene

oleic acid amide; vegetable oil ethers such as polyoxyethylene castor oil ether, and polyoxyethylene rapeseed oil ether; alkanol amides such as lauric acid diethanol amide, stearic acid diethanol amide, and oleic acid diethanol amide; and sorbitan ester ethers such as polyoxyethylene sorbitan monolaurate, polyoxyethylene sorbitan monopermylate, polyoxyethylene sorbitan monostearate, and polyoxyethylene sorbitan monooleate.

[0038]How to produce the toner is described next.

[0039]<Agglomeration Step>

In the agglomeration step, first, the above water base dispersion of first fine resin particles and water base dispersion of fine colorant particles, and also optionally a toner component(s) as exemplified by a release agent, are mixed to prepare an aqueous mixture. As a mixing machine therefor, a homogenizer, a mixer or the like may be used. Next, an agglomerating agent is added to and mixed in the aqueous mixture, and the particles contained in the aqueous mixture prepared are agglomerated at a temperature lower than the extrapolated glass transition onset temperature T_{gl} of the first resin to form an agglomerate. If agglomerated at a temperature not lower than T_{gl} , the rate of agglomeration rises so greatly as to consequently make it difficult to control particle diameter and make coarse particles tend to form. Also, the agglomeration step may preferably be carried out at a temperature higher than $T_{gl}-30(^{\circ}\text{C})$ and lower than T_{gl} , and much preferably be carried out at a temperature higher than $T_{gl}-20(^{\circ}\text{C})$ and lower than T_{gl} . Where the agglomeration step is carried out at a temperature higher than $T_{gl}-30(^{\circ}\text{C})$, the particle size distribution can be so controlled as to be sharp, and also the fine resin particles and the fine colorant particles can uniformly be agglomerated.

[0040]The release agent may include, e.g., low-molecular weight polyolefins such as polyethylene; silicones having melting point (softening point) by heating; fatty acid amides such as oleic acid amide, erucic acid amide, ricinolic acid amide and stearic acid amide; ester waxes such as stearyl stearate; vegetable waxes such as carnauba wax, rice wax, candelilla wax, japan wax and jojoba wax; animal waxes such as bees wax; mineral or petroleum waxes such as montan wax, ozokelite, serecin, paraffin wax, microcrystalline wax, Fischer-Tropsh wax and ester waxes; and modified products of these. The release agent may preferably be mixed in the form of a water base dispersion. Such a water base dispersion of the release agent may be prepared by adding the release agent to an aqueous medium containing a surface active agent, heating the resultant mixture to a temperature not lower than the melting point of the release agent and at the same time putting it to dispersion by means of a homogenizer having a strong shear-providing ability or a pressure ejection dispersion machine.

[0041]The agglomerating agent is a substance which makes unstable the fine particles standing dispersed in the aqueous mixture, to effect agglomeration. As the agglomerating agent, any known agents may be used, which may include, e.g., metal salts, surface active agents and organic solvents. Of these, metal salts are preferred, which promise easy control of particle diameter of the agglomerate and can readily be washed. Such metal salts may include, e.g., metal salts of monovalent metals such as sodium and potassium; metal salts of divalent metals such as calcium and magnesium; and metal salts of trivalent metals such as iron and aluminum.

[0042]As average particle diameter of the agglomerate formed here, there are no particular limitations thereon.

Usually, it may be so controlled that it may have substantially the same average particle diameter as the toner particles to be obtained. It can readily be controlled by, e.g., appropriately setting and changing the temperature at the time of adding and mixing the agglomerating agent and the conditions for the mixing by stirring.

[0043]<Primary Fusion Step>

The primary fusion step is the step of heating the water base dispersion containing the agglomerate, at a temperature not lower than the extrapolated glass transition end temperature T_{g1} of the first resin to fuse the agglomerate to obtain core particles the agglomerated particle surfaces of which have been made smooth. This step makes the agglomerated particles small in surface area, and makes shell particles efficiently adhere thereto in the adhering step detailed later. Before the primary fusion step is taken, a chelating agent, a pH adjuster, a surface active agent and/or the like may appropriately be introduced in order to prevent the core particles from fusing one another.

[0044]The chelating agent may include, as examples thereof, ethylenediaminetetraacetic acid (EDTA) and alkali metal salts such as sodium salts thereof, sodium gluconate, sodium tartrate, potassium citrate, sodium citrate, nitrotriacetate (NTA) salts, and water-soluble polymers (polymeric electrolytes) containing carboxylic acid groups or carboxylic acid metal bases in a large quantity.

[0045]As to temperature for the above heating, it may be any temperature between T_{g1} and the temperature at which the resin decomposes thermally. As to time for the heating and fusion, a shorter time may suffice as the heating temperature is higher, and a longer time is necessary as the heating temperature is lower. That is,

the time for heating and fusion depends on the temperature for heating, and hence it can not absolutely be defined, but may generally be from 10 minutes or more to 10 hours or less.

[0046]<Cooling Step>

The cooling step is the step of cooling the water base dispersion containing the core particles, to a temperature lower than T_{ig1} . If the cooling is not effected to the temperature lower than T_{ig1} , coarse particles may inevitably form when an agglomerating agent is added in the adhering step detailed later. The cooling may preferably be effected to a temperature lower by at least 6°C than T_{ig1} . As to cooling rate, it may preferably be from $0.1^{\circ}\text{C/minute}$ or more to $50^{\circ}\text{C/minute}$ or less.

[0047]<Adhering Step>

The adhering step is the step of mixing, at a temperature lower than T_{ig1} , a water base dispersion of second fine resin particles having a second resin and an agglomerating agent with the water base dispersion thus cooled and containing the core particles, to make the second fine resin particles adhere to the core particles to form a shell-adherent substance to obtain a water base dispersion of the shell-adherent substance. The adhering step is carried out next to the cooling step, and may preferably be carried out without filtering the core particles from this water base dispersion containing the core particles and also without being re-dispersed.

[0048]<Secondary Fusion Step>

The secondary fusion step is the step of heating the water base dispersion of the shell-adherent substance to a temperature not lower than T_{eg1} to fuse shells and core particles to thereby make particle surfaces smooth. As a result of the secondary fusion step, the core resin and the shell resin come sufficiently bound to

keep the shell resin from being liberated from the toner particles through operations such as washing and filtration which are described later. The temperature in the secondary fusion step may preferably be, as an upper limit value, $T_{eg1}+50^{\circ}\text{C}$ or less, and much preferably $T_{eg1}+30^{\circ}\text{C}$ or less, from the viewpoint of keeping the core particles component and the shells component from coming mixed in excess. Before the secondary fusion step is taken, a chelating agent, a pH adjuster, a surface active agent and/or the like may appropriately be introduced into the water base dispersion in order to prevent the toner particles from fusing one another.

[0049]As to temperature for the above heating, it may be T_{eg1} or more. Its upper limit value is the temperature at which the resin decomposes thermally. As to time for the heating and fusion, a shorter time may suffice as the heating temperature is higher, and a longer time is necessary as the heating temperature is lower. That is, the time for heating and fusion depends on the temperature for heating, and hence it can not absolutely be defined, but may generally be from 10 minutes or more to 10 hours or less.

[0050]The toner particles obtained after the secondary fusion step has been completed are cooled to room temperature, washed, filtered and then dried to obtain toner particles. Further, to the surfaces of the toner particles obtained, inorganic particles of silica, alumina, titania, calcium carbonate and the like, and resin particles of a vinyl resin, polyester resin, silicone resin and the like may be added by applying a shear force in a dry condition. Such inorganic particles and resin particles function as an external additive such as a fluidity assistant or a cleaning assistant.

[0051]The toner particles obtained according to the present

invention may preferably have a weight average particle diameter (D₄) of from 4.5 μm or more to 7.0 μm or less, and much preferably from 5.0 μm or more to 6.5 μm or less.

EXAMPLES

[0052] The present invention is described below in greater detail by giving working examples. Embodiments of the present invention are by no means limited to these. In the following formulation, "part(s)" is part(s) by mass unless particularly noted.

[0053] How to analyze various particles are described first.

[0054] <Measurement of Molecular Weight Distribution, Weight Average Molecular Weight (M_w) and Number Average Molecular Weight (M_n) of Resin by Gel Permeation Chromatography (GPC) of Tetrahydrofuran(THF)-soluble Matter>

The molecular weight distribution, weight average molecular weight (M_w) and number average molecular weight (M_n) of fine resin particles as measured by GPC of THF-soluble matter are determined in the following way.

[0055] Columns are stabilized in a heat chamber of 40°C. To the columns kept at this temperature, tetrahydrofuran (THF) as a solvent is flowed at a flow rate of 1 ml per minute, and about 100 μl of a sample THF solution is injected thereinto to make measurement. In measuring the molecular weight of the sample, the molecular weight distribution the sample has is calculated from the relationship between the logarithmic value of a calibration curve prepared using several kinds of monodisperse polystyrene standard samples and the number of count. The standard polystyrene samples (e.g., those with molecular weights of approximately from 100 or more to 10,000,000 or less, which are available from Tosoh Corporation or Showa Denko K.K.) for preparing the calibration curve are used, and it is

suitable to use at least about 10 standard polystyrene samples. An RI (refractive index) detector is used as a detector. Columns should be used in combination of a plurality of commercially available polystyrene gel columns. For example, they may preferably include a combination of columns Shodex GPC KF-801, KF-802, KF-803, KF-804, KF-805, KF-806, KF-807 and KF-800P, available from Showa Denko K.K.; and a combination of columns TSKgel G1000H(H_{XL}), G2000H(H_{XL}), G3000H(H_{XL}), G4000H(H_{XL}), G5000H(H_{XL}), G6000H(H_{XL}), G7000H(H_{XL}) and TSK guard column, available from Tosoh Corporation.

[0056]The sample is prepared in the following way.

[0057]The resin (sample) is put in tetrahydrofuran (THF), and is left for several hours, followed by thorough shaking so as to be well mixed with the THF (until any coalescent matter of the sample has disappeared), which is further left to stand for at least 12 hours. At this point, the sample is so left as to stand in THF for at least 24 hours. Thereafter, the solution having been passed through a sample treating filter (pore size: from 0.45 μm or more to 0.5 μm or less; e.g., MAISHORIDISK H-25-5, available from Tosoh Corporation, EKI KURODISK 25CR, available from German Science Japan, Ltd., may be used) is used as the sample for GPC. The sample is so adjusted as to have resin components in a concentration of from 0.5 mg/ml or more to 5 mg/ml or less.

[0058]<Measurement of Acid Value of Resin>

The acid value of the resins each is determined in the following way. Basic operation is made according to JIS (Japanese Industrial Standards) K0070. The acid value refers to the number of milligrams of potassium hydroxide necessary to neutralize free fatty acid, resin acid and the like contained in 1 g of a sample.

[0059](1) Reagent

(a) Solvent: An ethyl ether/ethyl alcohol mixture

solution (1+1 or 2+1) or a benzene/ethyl alcohol mixture solution (1+1 or 2+1) is, immediately before use, kept neutralized with a 0.1 mol/litter potassium hydroxide ethyl alcohol solution using phenolphthalein as an indicator.

(b) Phenolphthalein solution: 1 g of phenolphthalein is dissolved in 100 ml of ethyl alcohol (95 v/v%).

(c) 0.1 mol/litter potassium hydroxide/ethyl alcohol solution: 7.0 g of potassium hydroxide is dissolved in water used in a quantity as small as possible, and ethyl alcohol (95 v/v%) is added thereto to make up a 1 liter solution, which is then left to stand for 2 or 3 days, followed by filtration. Standardization is made according to JIS (Japanese Industrial Standards) K8006 (basic items relating to titration during a reagent content test).

[0060] (2) Operation

From 1 g or more to 20 g or less of the resin (sample) is precisely weighed out, and 100 ml of the solvent and few drops of the phenolphthalein solution as an indicator are added thereto, which are then thoroughly shaken until the sample dissolves completely. In the case of a solid sample, it is dissolved by heating on a water bath. After cooling, the resultant solution is titrated with the 0.1 mol/litter potassium hydroxide ethyl alcohol solution, and the time by which the indicator has stood sparingly red for 30 seconds is regarded as the end point of neutralization.

[0061] (3) Calculation

Acid value is calculated from the following equation.

$$A = (B \times f \times 5.611) / S$$

where;

A: acid value;

B: the amount (ml) of the 0.1 mol/litter potassium hydroxide ethyl alcohol solution used;

f: the factor of the 0.1 mol/litter potassium hydroxide

ethyl alcohol solution; and

S: mass of the sample (g).

[0062]<Analysis of Particle Size Distribution of Fine Resin Particles, Fine Colorant Particles and Fine Release Agent Particles>

The particle size distribution is analyzed with a laser diffraction/scattering particle size distribution measuring instrument (LA-950, Horiba Ltd.), and is measured according to an operation manual attached to the instrument. An aqueous surface active agent solution is dropwise added to circulating water, and the fine resin particles dispersion or fine colorant particles dispersion or fine release agent particles dispersion is dropwise added until it comes to be in optimum concentration for the instrument, dispersion is carried out for 30 seconds by using ultrasonic waves, and the measurement is started to determine volume base median diameter and volume base 95% particle diameter (D95).

[0063]<Analysis of Particle Size Distribution of Toner Particles>

The particle size distribution of the toner particles are measured by particle size distribution analysis according to the Coulter method. COULTER COUNTER TA-II or COULTER MULTISIZER II (Beckman Coulter, Inc.) is used as a measuring instrument, and measurement is made according to an operation manual attached to the instrument. As an electrolytic solution, an about-1% sodium chloride solution is prepared using first-grade sodium chloride. For example, ISOTON-II (Coulter Scientific Japan Co.) may be used as the electrolytic solution. As a specific measuring method, from 0.1 ml or more to 5 ml or less of a surface active agent (preferably an alkylbenzenesulfonate) is added as a dispersant to from 100 ml or more to 150 ml or less of the above aqueous electrolytic solution, and from 2 mg

or more to 20 mg or less of a sample (toner particles) for measurement is further added. The electrolytic solution in which the sample has been suspended is subjected to dispersion treatment from about 1 minute or more to about 3 minutes or less in an ultrasonic dispersion machine. The dispersion-treated suspension obtained is put in the above measuring instrument, fitted with an aperture of 100 μm as its aperture, by means of which the volume and number of toner particles of 2.00 μm or more in diameter are measured, and then the volume distribution and number distribution are calculated. From the results of calculation, the weight average particle diameter (D4) of the toner particles is found, and further the amount of coarse particles is found from the proportion (%) by number of particles larger than 10 μm .

[0064] (Production Example 1)

0.15 g of an anionic surface active agent (NEOGEN RK, Dai-ichi Kogyo Seiyaku Co., Ltd.) and 3.15 g of N,N-dimethylaminoethanol (a basic substance) were dissolved in 146.70 g of ion-exchanged water (an aqueous medium) to prepare a dispersion medium solution. This dispersion medium solution was put into a 350 ml pressure round-bottomed stainless steel container, and then 150 g of a pulverized product (from 1 mm or more to 2 mm or less in diameter) of "polyester resin A" [composed of polyoxypropylene(2.2)-2,2-bis(4-hydroxyphenyl)propane:polyoxyethylene(2.0)-2,2-bis(4-hydroxyphenyl)propane:terephthalic acid:fumaric acid:trimellitic acid = 25:25:26:20:4 (molar ratio), Mn: 3,500, Mw: 10,300, Mw/Mn: 2.9, Tm: 96°C, Tig: 53°C, Teg: 58°C] was introduced thereinto, followed by mixing.

[0065] Next, a high-speed shearing emulsifying apparatus

CLEAMIX (CLM-2.2S, M_{TECHNIQUE} Co., Ltd.) was hermetically connected to the above pressure round-bottomed stainless steel container. The mixture in the

container was put to shearing dispersion for 30 minutes under application of heat and pressure of 115°C and 0.18 MPa, setting the number of revolutions of the rotor of CLEAMIX to 18,000 r/minute. Thereafter, while maintaining its revolution at 18,000 r/minute, the dispersed product was cooled at a cooling rate of 2.0°C/minute until it came to 50°C, to obtain a water base dispersion 1 of fine resin particles. Electron microscopic observation (10,000 magnifications) revealed that the fine resin particles had a breadth of 0.22 µm on the average and a length of 0.56 µm on the average and a length/breadth ratio of 2.72 on the average, where proportion of particles having a length/breadth ratio in the range of from 1.5 or more to 10 or less accounted for 98% of the whole. The fine resin particles also had a volume distribution base median diameter (D50) of 0.22 µm and volume base 95% particle diameter (D95) of 0.27 µm as measured with a laser diffraction/scattering particle size distribution measuring instrument (LA-950, Horiba Ltd.).

[0066] (Production Example 2)

0.15 g of an anionic surface active agent (NEOGEN RK, Dai-ichi Kogyo Seiyaku Co., Ltd.) and 3.15 g of N,N-dimethylaminoethanol (a basic substance) were dissolved in 146.70 g of ion-exchanged water (an aqueous medium) to prepare a dispersion medium solution. This dispersion medium solution was put into a 350 ml pressure round-bottomed stainless steel container, and then 150 g of a pulverized product (from 1 mm or more to 2 mm or less in diameter) of "polyester resin B" [composed of polyoxypropylene(2.2)-2,2-bis(4-hydroxyphenyl)propane:polyoxyethylene(2.0)-2,2-bis(4-hydroxyphenyl)propane:terephthalic acid:fumaric acid:trimellitic acid = 25:25:26:20:4 (molar ratio), Mn: 4,000, Mw: 13,000, Mw/Mn: 3.3, Tm: 105°C, Tig: 53°C, Teg: 59°C] was introduced thereinto, followed by mixing.

[0067]Next, a high-speed shearing emulsifying apparatus CLEAMIX (CLM-2.2S, M_{TECHNIQUE} Co., Ltd.) was hermetically connected to the above pressure round-bottomed stainless steel container. The mixture in the container was put to shearing dispersion for 30 minutes under application of heat and pressure of 125°C and 0.24 MPa, setting the number of revolutions of the rotor of CLEAMIX to 18,000 r/minute. Thereafter, while maintaining its revolution at 18,000 r/minute, the dispersed product was cooled at a cooling rate of 2.0°C/minute until it came to 50°C, to obtain a water base dispersion 2 of fine resin particles. Electron microscopic observation (10,000 magnifications) revealed that the fine resin particles had a breadth of 0.24 µm on the average and a length of 0.61 µm on the average and a length/breadth ratio of 2.54 on the average, where proportion of particles having a length/breadth ratio in the range of from 1.5 or more to 10 or less accounted for 98% of the whole. The fine resin particles also had a volume distribution base median diameter (D50) of 0.25 µm and volume base 95% particle diameter (D95) of 0.30 µm as measured with a laser diffraction/scattering particle size distribution measuring instrument (LA-950, Horiba Ltd.).

[0068](Production Example 3)

0.15 g of an anionic surface active agent (NEOGEN RK, Dai-ichi Kogyo Seiyaku Co., Ltd.) and 3.15 g of N,N-dimethylaminoethanol (a basic substance) were dissolved in 146.70 g of ion-exchanged water (an aqueous medium) to prepare a dispersion medium solution. This dispersion medium solution was put into a 350 ml pressure round-bottomed stainless steel container, and then 150 g of a pulverized product (from 1 mm or more to 2 mm or less in diameter) of "polyester resin C" [composed of polyoxypropylene(2.2)-2,2-bis(4-hydroxyphenyl)propane:polyoxyethylene(2.0)-2,2-bis(4-

hydroxyphenyl)propane:terephthalic acid:fumaric acid:trimellitic acid = 25:25:26:20:4 (molar ratio), Mn: 2,800, Mw: 9,500, Mw/Mn: 3.4, Tm: 80°C, Tig: 51°C, Teg: 57°C] was introduced thereinto, followed by mixing.

[0069] Next, a high-speed shearing emulsifying apparatus CLEAMIX (CLM-2.2S, M_{TECHNIQUE} Co., Ltd.) was hermetically connected to the above pressure round-bottomed stainless steel container. The mixture in the container was put to shearing dispersion for 30 minutes under application of heat and pressure of 115°C and 0.18 MPa, setting the number of revolutions of the rotor of CLEAMIX to 18,000 r/minute. Thereafter, while maintaining its revolution at 18,000 r/minute, the dispersed product was cooled at a cooling rate of 2.0°C/minute until it came to 50°C, to obtain a water base dispersion 3 of fine resin particles. Electron microscopic observation (10,000 magnifications) revealed that the fine resin particles had a breadth of 0.20 µm on the average and a length of 0.51 µm on the average and a length/breadth ratio of 2.55 on the average, where proportion of particles having a length/breadth ratio in the range of from 1.5 or more to 10 or less accounted for 98% of the whole. The fine resin particles also had a volume distribution base median diameter (D50) of 0.21 µm and volume base 95% particle diameter (D95) of 0.26 µm as measured with a laser diffraction/scattering particle size distribution measuring instrument (LA-950, Horiba Ltd.).

[0070] (Production Example 4)

0.15 g of an anionic surface active agent (NEOGEN RK, Dai-ichi Kogyo Seiyaku Co., Ltd.) and 3.15 g of N,N-dimethylaminoethanol (a basic substance) were dissolved in 146.70 g of ion-exchanged water (an aqueous medium) to prepare a dispersion medium solution. This dispersion medium solution was put into a 350 ml pressure round-bottomed stainless steel container, and

then 150 g of a pulverized product (from 1 mm or more to 2 mm or less in diameter) of "polyester resin D" [composed of polyoxypropylene(2.2)-2,2-bis(4-hydroxyphenyl)propane:polyoxyethylene(2.0)-2,2-bis(4-hydroxyphenyl)propane:terephthalic acid:fumaric acid:trimellitic acid = 25:25:26:18:6 (molar ratio), Mn: 5,000, Mw: 35,000, Mw/Mn: 7.0, Tm: 115°C, Tig: 55°C, Teg: 61°C] was introduced thereinto, followed by mixing.

[0071] Next, a high-speed shearing emulsifying apparatus CLEAMIX (CLM-2.2S, M_{TECHNIQUE} Co., Ltd.) was hermetically connected to the above pressure round-bottomed stainless steel container. The mixture in the container was put to shearing dispersion for 30 minutes under application of heat and pressure of 135°C and 0.32 MPa, setting the number of revolutions of the rotor of CLEAMIX to 18,000 r/minute. Thereafter, while maintaining its revolution at 18,000 r/minute, the dispersed product was cooled at a cooling rate of 2.0°C/minute until it came to 50°C, to obtain a water base dispersion 4 of fine resin particles. Electron microscopic observation (10,000 magnifications) revealed that the fine resin particles had a breadth of 0.25 µm on the average and a length of 0.62 µm on the average and a length/breadth ratio of 2.48 on the average, where proportion of particles having a length/breadth ratio in the range of from 1.5 or more to 10 or less accounted for 98% of the whole. The fine resin particles also had a volume distribution base median diameter (D50) of 0.25 µm and volume base 95% particle diameter (D95) of 0.31 µm as measured with a laser diffraction/scattering particle size distribution measuring instrument (LA-950, Horiba Ltd.).

[0072] (Production Example 5)

0.90 g of an anionic surface active agent (NEOGEN RK, Dai-ichi Kogyo Seiyaku Co., Ltd.) and 1.57 g of N,N-dimethylaminoethanol (a basic substance) were dissolved

in 207.53 g of ion-exchanged water (an aqueous medium) to prepare a dispersion medium solution. This dispersion medium solution was put into a 350 ml pressure round-bottomed stainless steel container, and then 90 g of the pulverized product (from 1 mm or more to 2 mm or less in diameter) of "polyester resin A" was introduced thereinto, followed by mixing. Next, a water base dispersion 5 of fine resin particles was obtained in the same way as in Production Example 1 except above procedure. Electron microscopic observation (10,000 magnifications) revealed that the fine resin particles had a breadth of 0.66 μm on the average and a length of 1.95 μm on the average and a length/breadth ratio of 2.95 on the average, where proportion of particles having a length/breadth ratio in the range of from 1.5 or more to 10 or less accounted for 98% of the whole. The fine resin particles also had a volume distribution base median diameter (D50) of 0.67 μm and volume base 95% particle diameter (D95) of 0.97 μm as measured with a laser diffraction/scattering particle size distribution measuring instrument (LA-950, Horiba Ltd.).

[0073] (Production Example 6)

1.50 g of an anionic surface active agent (NEOGEN RK, Dai-ichi Kogyo Seiyaku Co., Ltd.) and 5.26 g of N,N-dimethylaminoethanol (a basic substance) were dissolved in 143.24 g of ion-exchanged water (an aqueous medium) to prepare a dispersion medium solution. This dispersion medium solution was put into a 350 ml pressure round-bottomed stainless steel container, and then 150 g of the pulverized product (from 1 mm or more to 2 mm or less in diameter) of "polyester resin A" was introduced thereinto, followed by mixing. Next, a water base dispersion 6 of fine resin particles was obtained in the same way as in Production Example 1 except above procedure. Electron microscopic

observation (10,000 magnifications) revealed that the fine resin particles had a breadth of 0.11 μm on the average and a length of 0.30 μm on the average and a length/breadth ratio of 2.73 on the average, where proportion of particles having a length/breadth ratio in the range of from 1.5 or more to 10 or less accounted for 98% of the whole. The fine resin particles also had a volume distribution base median diameter (D50) of 0.11 μm and volume base 95% particle diameter (D95) of 0.17 μm as measured with a laser diffraction/scattering particle size distribution measuring instrument (LA-950, Horiba Ltd.).

[0074] (Production Example 7)

Polyester resin A	60 g
Anionic surface active agent (NEOGEN RK, Dai-ichi Kogyo Seiyaku Co., Ltd.)	0.3 g
N,N-dimethylaminoethanol	1.5 g
Tetrahydrofuran	200 g

The above components were mixed and dissolved, and then stirred by means of a high-speed stirring apparatus (T.K. ROBOMIX, PRIMIX Corporation) at 4,000 r/minute. Further, 180 g of ion-exchanged water was dropwise added thereto, and thereafter the tetrahydrofuran was removed by means of an evaporator to obtain a water base dispersion 7 of fine resin particles. Electron microscopic observation (20,000 magnifications) revealed that the fine resin particles were spherical as having a breadth of 0.18 μm on the average and a length of 0.19 μm on the average and a length/breadth ratio of 1.05 on the average, where particles having a length/breadth ratio smaller than 1.5 accounted for 100% of the whole. The fine resin particles also had a volume distribution base median diameter (D50) of 0.18 μm and volume base 95% particle diameter (D95) of 0.25 μm as measured with a laser diffraction/scattering particle size distribution measuring instrument (LA-950,

Horiba Ltd.).

[0075] (Production Example 8)

Styrene	350 g
n-Butyl acrylate	125 g
Acrylic acid	3 g
n-Dodecyl mercaptan	10 g

The above components were mixed to prepare a monomer solution. An aqueous surface active agent solution prepared by dissolving 10 g of an anionic surface active agent (NEOGEN RK, Dai-ichi Kogyo Seiyaku Co., Ltd.) in 1,130 g of ion-exchanged water and the monomer solution were put into a two-necked flask, and then stirred by means of a homogenizer (ULTRATALUX T50, IKA Works, Inc.) at a number of revolutions of 10,000 r/minute to effect emulsification. Thereafter, the inside of the flask was displaced with nitrogen, and then its contents were heated in a water bath with gentle stirring until they came to 70°C, and thereafter 350 g of ion-exchanged water in which 6.56 g of ammonium persulfate was dissolved was introduced thereinto to initiate polymerization. After the reaction was continued for 6 hours, the reaction mixture obtained was cooled to room temperature to obtain a water base dispersion 8 of fine resin particles. The resin obtained had Tig of 53°C, Teg of 59°C, Tm of 100°C, Mw of 13,000, Mw/Mn of 2.6 and Mp of 9,900. Electron microscopic observation (20,000 magnifications) revealed that the fine resin particles were spherical as having a breadth of 0.19 μm on the average and a length of 0.20 μm on the average and a length/breadth ratio of 1.05 on the average, where particles having a length/breadth ratio smaller than 1.5 accounted for 100% of the whole. The fine resin particles also had a volume distribution base median diameter (D50) of 0.19 μm and volume base 95% particle diameter (D95) of 0.27 μm as measured with a laser

diffraction/scattering particle size distribution measuring instrument (LA-950, Horiba Ltd.).

[0076] (Production Example 9)

Polyester resin E 60 g
(composed of polyoxypropylene(2.2)-2,2-bis(4-hydroxyphenyl)propane:ethylene glycol:terephthalic acid:maleic acid:trimellitic acid = 35:15:33:15:2 (molar ratio), Mn: 4,600, Mw: 16,500, Mp: 10,400, Mw/Mn: 3.6, Tig: 64°C, Teg: 70°C, acid value: 13 mgKOH/g)

Anionic surface active agent 0.3 g
(NEOGEN RK, Dai-ichi Kogyo Seiyaku Co., Ltd.)

N,N-dimethylaminoethanol 1.5 g

Tetrahydrofuran 200 g

The above components were mixed and dissolved, and then stirred by means of a high-speed stirring apparatus (T.K. ROBOMIX, PRIMIX Corporation) at 4,000 r/minute. Further, 180 g of ion-exchanged water was dropwise added thereto to obtain a water base dispersion 9 of fine resin particles. The fine resin particles had a volume distribution base median diameter (D50) of 0.18 μm and volume base 95% particle diameter (D95) of 0.25 μm as measured with a laser diffraction/scattering particle size distribution measuring instrument (LA-950, Horiba Ltd.).

[0077] (Production Example 10)

A water base dispersion 10 of fine resin particles was obtained in the same way as in Production Example 9 except that the amount 1.5 g of the N,N-dimethylaminoethanol was changed to 1.8 g. The fine resin particles had a volume distribution base median diameter (D50) of 0.06 μm and volume base 95% particle diameter (D95) of 0.09 μm as measured with a laser diffraction/scattering particle size distribution measuring instrument (LA-950, Horiba Ltd.).

[0078] (Production Example 11)

A water base dispersion 11 of fine resin particles was obtained in the same way as in Production Example 9 except that the amount 1.5 g of the N,N-dimethylaminoethanol was changed to 1.3 g. The fine resin particles had a volume distribution base median diameter (D50) of 0.29 μm and volume base 95% particle diameter (D95) of 0.36 μm as measured with a laser diffraction/scattering particle size distribution measuring instrument (LA-950, Horiba Ltd.).

[0079] (Production Example 12)

A water base dispersion 12 of fine resin particles was obtained in the same way as in Production Example 9 except that the amount 1.5 g of the N,N-dimethylaminoethanol was changed to 1.1 g. The fine resin particles had a volume distribution base median diameter (D50) of 0.35 μm and volume base 95% particle diameter (D95) of 0.45 μm as measured with a laser diffraction/scattering particle size distribution measuring instrument (LA-950, Horiba Ltd.).

[0080] (Production Example 13)

Polyester resin F 60 g
(composed of polyoxypropylene(2.2)-2,2-bis(4-hydroxyphenyl)propane:ethylene glycol:terephthalic acid:maleic acid:trimellitic acid = 35:15:40:8:2 (molar ratio), Mn: 4,800, Mw: 17,500, Mw/Mn: 3.6, Tig: 72°C, Teg: 78°C)

Anionic surface active agent 0.3 g
(NEOGEN RK, Dai-ichi Kogyo Seiyaku Co., Ltd.)

N,N-dimethylaminoethanol 1.5 g

Tetrahydrofuran 200 g

The above components were mixed, and then a water base dispersion 13 of fine resin particles was obtained in the same way as in Production Example 9. The fine resin particles had a volume distribution base median diameter (D50) of 0.19 μm and volume base 95% particle diameter (D95) of 0.28 μm as measured with a laser

diffraction/scattering particle size distribution
measuring instrument (LA-950, Horiba Ltd.).

[0081] (Production Example 14)

Polyester resin G	60 g
(composed of polyoxypropylene(2.2)-2,2-bis(4-hydroxyphenyl)propane:ethylene glycol:terephthalic acid:maleic acid:trimellitic acid = 35:15:27:21:2 (molar ratio), Mn: 4,200, Mw: 15,100, Mw/Mn: 3.6, Tig: 58°C, Teg: 64°C)	
Anionic surface active agent (NEOGEN RK, Dai-ichi Kogyo Seiyaku Co., Ltd.)	0.3 g
N,N-dimethylaminoethanol	1.5 g
Tetrahydrofuran	200 g

The above components were mixed, and then a water base dispersion 14 of fine resin particles was obtained in the same way as in Production Example 9. The fine resin particles had a volume distribution base median diameter (D50) of 0.17 μm and volume base 95% particle diameter (D95) of 0.23 μm as measured with a laser diffraction/scattering particle size distribution measuring instrument (LA-950, Horiba Ltd.).

[0082] (Production Example 15)

Styrene	400 g
n-Butyl acrylate	100 g
Acrylic acid	3 g
n-Dodecyl mercaptan	5 g

The above components were mixed to prepare a monomer solution. An aqueous surface active agent solution prepared by dissolving 10 g of an anionic surface active agent (NEOGEN RK, Dai-ichi Kogyo Seiyaku Co., Ltd.) in 1,130 g of ion-exchanged water and the monomer solution were put into a two-necked flask, and then stirred by means of a homogenizer (ULTRATALUX T50, IKA Works, Inc.) at a number of revolutions of 10,000 r/minute to effect emulsification. Thereafter, the inside of the flask was displaced with nitrogen, and

then its contents were heated in a water bath with gentle stirring until they came to 70°C, and thereafter 350 parts of ion-exchanged water in which 6.56 g of ammonium persulfate was dissolved was introduced thereinto to initiate polymerization. After the reaction was continued for 7 hours, the reaction mixture obtained was cooled to room temperature to obtain a water base dispersion 15 of fine resin particles. The resin obtained had Tig of 63°C, Teg of 69°C, Mw of 26,000 and Mw/Mn of 2.5. The fine resin particles had a volume distribution base median diameter (D50) of 0.17 µm and volume base 95% particle diameter (D95) of 0.24 µm as measured with a laser diffraction/scattering particle size distribution measuring instrument (LA-950, Horiba Ltd.).

[0083] (Production Example 16)

Using the polyester resin E, this was so pulverized as to have a maximum particle diameter of 100 µm or less to obtain a resin pulverized product having a volume distribution base 50% particle diameter of 18 µm. Then, 100 g of this resin pulverized product was mixed with 900 g of ion-exchanged water to which 10 g of an anionic surface active agent (NEOGEN RK, Dai-ichi Kogyo Seiyaku Co., Ltd.) was added. To the mixture obtained, 7.1 g of N,N-diethylaminoethanol was further added. Thereafter, this mixture was brought into a high-pressure impact dispersion machine Nanomizer (Yoshida Kikai Co., Ltd.) and, just before treatment at its treating section, was heated to 180°C and then introduced into the treating section (generator), where emulsification treatment was carried out five times at 200 MPa to obtain a water base dispersion 16 of fine polyester resin particles. The fine resin particles had a volume distribution base median diameter (D50) of 0.26 µm and volume base 95% particle diameter (D95) of 0.35 µm as measured with a laser diffraction/scattering

particle size distribution measuring instrument (LA-950, Horiba Ltd.).

[0084] Values of physical properties of the fine resin particles obtained according to Production Examples 1 to 16 are shown in Table 1.

Table 1

Production Example	Water base dispersion		Physical properties of fine resin particles contained in water base dispersion						Proportion of length/breadth ratio of 1.5 to 10 (% by number)
	No.	Solid matter conc. (ms.%)	Type of resin	D50 (μm)	D95 (μm)	Breadth (μm)	Length (μm)	Breadth /length ratio	
1	1	50.0	Polyester A	0.22	0.27	0.22	0.56	2.72	98
2	2	50.0	Polyester B	0.25	0.30	0.24	0.61	2.54	98
3	3	50.0	Polyester C	0.21	0.26	0.20	0.51	2.55	98
4	4	50.0	Polyester D	0.25	0.31	0.25	0.62	2.48	98
5	5	50.0	Polyester A	0.67	0.97	0.66	1.95	2.95	98
6	6	50.0	Polyester A	0.11	0.17	0.11	0.30	2.73	98
7	7	24.8	Polyester A	0.18	0.25	0.18	0.19	1.05	0
8	8	24.3	Vinyl resin	0.19	0.27	0.19	0.20	1.05	0
9	9	24.8	Polyester E	0.18	0.25	-	-	-	-
10	10	24.8	Polyester E	0.06	0.09	-	-	-	-
11	11	24.8	Polyester E	0.29	0.36	-	-	-	-
12	12	24.9	Polyester E	0.35	0.45	-	-	-	-
13	13	24.8	Polyester F	0.19	0.28	-	-	-	-
14	14	24.8	Polyester G	0.17	0.23	-	-	-	-
15	15	25.2	Vinyl resin	0.17	0.24	-	-	-	-
16	16	9.8	Polyester E	0.26	0.35	-	-	-	-

[0085] (Water Base Dispersion of Fine Colorant Particles)

Cyan pigment, C.I. Pigment Blue 15:3	100 g
(Dainichiseika Color & Chemicals Co., Ltd.)	
Anionic surface active agent	15 g
(NEOGEN RK, Dai-ichi Kogyo Seiyaku Co., Ltd.)	
Ion-exchanged water	885 g

The above components were mixed and dissolved, and then put to dispersion for 1 hour by means of a high-pressure impact dispersion machine Nanomizer (Yoshida Kikai Co., Ltd.) to prepare a water base dispersion of fine colorant particles, in which the colorant stood dispersed (solid matter concentration: 10% by mass). The fine colorant particles had a volume distribution base median diameter of 0.2 μm .

[0086] (Water Base Dispersion of Fine Release Agent Particles)

Ester wax	100 g
(behenyl behenate; melting point: 75°C)	
Anionic surface active agent	10 g
(NEOGEN RK, Dai-ichi Kogyo Seiyaku Co., Ltd.)	
Ion-exchanged water	880 g

The above components were introduced into a mixing container provided with a stirrer, and thereafter heated to 90°C. Then, these were put into CLEAMIX W-Motion (M_{TECHNIQUE} Co., Ltd.) and, with circulation, stirred at its shear stirring portion of 3 cm in rotor external diameter and 0.3 mm in clearance under conditions of a number of revolutions of rotor of 19,000 r/minute and a number of revolutions of screen of 19,000 r/minute to carry out dispersion treatment for about 60 minutes, and thereafter cooled to 40°C under cooling conditions of a number of revolutions of rotor of 1,000 r/minute, a number of revolutions of screen of 0 r/minute and a cooling rate of 10°C/minute to obtain a water base dispersion of fine release agent particles (solid matter concentration: 10% by mass). The fine release agent particles had a volume

distribution base median diameter of 0.15 μm .

[0087]<Example 1>

Water base dispersion 1 of fine resin particles
40.0 g

Water base dispersion of fine colorant particles
10.0 g

Water base dispersion of fine release agent particles
20.0 g

Aqueous 1% by mass calcium chloride solution 20.0 g

Ion-exchanged water 110.0 g

The above components were mixed and dispersed by using a homogenizer (ULTRATALUX T50, IKA Works, Inc.), and thereafter heated to 45°C in a water bath with stirring by means of a stirring blade. After retention at 45°C for 1 hour, the dispersion obtained was observed on an optical microscope, where it was ascertained that agglomerated particles having an average particle diameter of about 5.5 μm stood formed (the agglomeration step). After addition of 40.0 g of an aqueous 5% by mass trisodium citrate solution, the resultant mixture was heated to 85°C with stirring continued, and this was retained for 120 minutes to obtain a water base dispersion containing core particles formed of agglomerated particles having been fused (the primary fusion step). The particle diameter of the core particles was measured to find that their weight average particle diameter (D4) was 5.5 μm .

[0088]Next, with stirring continued, water was put into the water bath, where the water base dispersion of core particles was cooled to 25°C (the cooling step). Next, 12.1 g of the water base dispersion 9 of fine resin particles was added thereto. Thereafter, the mixture obtained was stirred for 10 minutes, and further 60.0 g of an aqueous 2% by mass calcium chloride solution was dropwise added thereto, and these were heated to 35°C. In this state, the liquid was taken out in a small

quantity as occasion called, and was passed through a microfilter of 2 μm in pore size, where the stirring was continued at 35°C until the filtrate became transparent (the adhering step). After it was made sure that the filtrate became transparent, the fine resin particles adhered to the core particles and a shell-adherent substance was formed, a water base dispersion of the shell-adherent substance was heated to 40°C, and then stirred for 1 hour, followed by addition of 35.0 g of an aqueous 5% by mass trisodium citrate solution to carry out stirring for 1.5 hours with heating to 65°C (the secondary fusion step). Thereafter, the liquid obtained was cooled to 25°C, and thereafter filtered to effect solid-liquid separation, followed by addition of 800 g of ion-exchanged water to the solid matter to carry out stirring and washing for 30 minutes. Thereafter, the solid-liquid separation was again effected. Thus, filtration and washing were repeated until the filtrate came to have an electrical conductivity of 150 $\mu\text{S}/\text{cm}$, in order to eliminate any influence of a residual surface active agent. The solid matter obtained was dried to obtain toner particles 1. The toner particles 1 had a weight average particle diameter (D_4) of 5.9 μm . In 100 parts of the toner particles thus obtained, 1.8 parts of hydrophobic-treated fine silica powder having a specific surface area of 200 m^2/g as measured by the BET method was mixed by a dry process by means of Henschel mixer (Mitsui Mining & Smelting Co. Ltd.) to obtain a toner 1.

[0089]<Examples 2 to 11>

Toners 2 to 11 were obtained in the same way as in Example 1 except that the types and amounts of the water base dispersions were changed as shown in Table 2.

[0090]<Example 12>

Water base dispersion 5 of fine resin particles

	66.6 g
Water base dispersion of fine colorant particles	
	10.0 g
Water base dispersion of fine release agent particles	
	20.0 g
Aqueous 1% by mass calcium chloride solution	20.0 g
Ion-exchanged water	83.4 g

The above components were put to dispersion by using a homogenizer (ULTRATALUX T50, IKA Works, Inc.). The subsequent procedure of Example 1 was repeated to produce toner particles 12 to obtain a toner 12.

[0091]<Example 13>

A toner 13 was obtained in the same way as in Example 1 except that the types and amounts of the water base dispersions were changed as shown in Table 2.

[0092]<Example 14>

Water base dispersion 7 of fine resin particles	
	80.5 g
Water base dispersion of fine colorant particles	
	10.0 g
Water base dispersion of fine release agent particles	
	20.0 g
Aqueous 1% by mass calcium chloride solution	20.0 g
Ion-exchanged water	69.5 g

The above components were put to dispersion by using a homogenizer (ULTRATALUX T50, IKA Works, Inc.). The subsequent procedure of Example 1 was repeated to produce toner particles 14 to obtain a toner 14.

[0093]<Example 15>

Water base dispersion 8 of fine resin particles	
	82.5 g
Water base dispersion of fine colorant particles	
	10.0 g
Water base dispersion of fine release agent particles	
	20.0 g
Aqueous 1% by mass calcium chloride solution	20.0 g

Ion-exchanged water 67.5 g

The above components were put to dispersion by using a homogenizer (ULTRATALUX T50, IKA Works, Inc.), and thereafter heated to 45°C in a water bath with stirring by means of a stirring blade. After retention at 45°C for 1 hour, the dispersion obtained was observed on an optical microscope, where it was ascertained that agglomerated particles having an average particle diameter of about 5.6 µm stood formed. After addition of 40.0 g of an aqueous 5% by mass trisodium citrate solution, the resultant mixture was heated to 85°C with stirring continued, and this was retained for 120 minutes to obtain a water base dispersion containing core particles formed of agglomerated particles having been fused. The particle diameter of the core particles was measured to find that their weight average particle diameter (D4) was 5.6 µm.

[0094]Next, with stirring continued, water was put into the water bath, where the water base dispersion of core particles was cooled to 25°C. Next, 11.9 g of the water base dispersion 15 of fine resin particles was added thereto. The subsequent procedure of Example 1 was repeated to produce toner particles 15 to obtain a toner 15.

[0095]<Example 16>

Water base dispersion 1 of fine resin particles

40.0 g

Water base dispersion of fine colorant particles

10.0 g

Water base dispersion of fine release agent particles

20.0 g

Aqueous 1% by mass calcium chloride solution 20.0 g

Ion-exchanged water 110.0 g

The above components were put to dispersion by using a homogenizer (ULTRATALUX T50, IKA Works, Inc.), and thereafter heated to 45°C in a water bath with stirring

by means of a stirring blade. After retention at 45°C for 1 hour, the dispersion obtained was observed on an optical microscope, where it was ascertained that agglomerated particles having an average particle diameter of about 5.5 μm stood formed. After addition of 40.0 g of an aqueous 5% by mass trisodium citrate solution, the resultant mixture was heated to 85°C with stirring continued, and this was retained for 120 minutes to obtain a water base dispersion containing core particles formed of agglomerated particles having been fused. The particle diameter of the core particles was measured to find that their weight average particle diameter (D_4) was 5.5 μm .

[0096]Next, with stirring continued, water was put into the water bath, where the water base dispersion of core particles was cooled to 45°C. Next, 12.1 g of the water base dispersion 9 of fine resin particles was added thereto. Thereafter, the mixture obtained was stirred for 10 minutes, and further 60 g of an aqueous 2% by mass calcium chloride solution was dropwise added thereto. In this state, the liquid was taken out in a small quantity as occasion called, and was passed through a microfilter of 2 μm in pore size, where the stirring was continued at 45°C until the filtrate became transparent. After it was made sure that the filtrate became transparent, the product was further stirred for 1 hour. The subsequent procedure of Example 1 was repeated to produce toner particles 16 to obtain a toner 16.

[0097]<Example 17>

A toner 17 was obtained in the same way as in Example 1 except that the types and amounts of the water base dispersions were changed as shown in Table 2.

[0098]<Example 18>

Water base dispersion 1 of fine resin particles

40.0 g

Water base dispersion of fine colorant particles
10.0 g

Water base dispersion of fine release agent particles
20.0 g

Aqueous 1% by mass calcium chloride solution 20.0 g

Ion-exchanged water 110.0 g

The above components were put to dispersion by using a homogenizer (ULTRATALUX T50, IKA Works, Inc.), and thereafter heated to 45°C in a water bath with stirring by means of a stirring blade. After retention at 45°C for 1 hour, the dispersion obtained was observed on an optical microscope, where it was ascertained that agglomerated particles having an average particle diameter of about 5.5 μm stood formed. After addition of 40 g of an aqueous 5% by mass trisodium citrate solution, the resultant mixture was heated to 85°C with stirring continued, and this was retained for 120 minutes to obtain a water base dispersion containing core particles formed of agglomerated particles having been fused. The particle diameter of the core particles was measured to find that their weight average particle diameter (D4) was 5.5 μm .

[0099] Next, with stirring continued, water was put into the water bath, where the water base dispersion of core particles was cooled to 51°C. Next, 12.1 g of the water base dispersion 9 of fine resin particles was added thereto. Thereafter, the mixture obtained was stirred for 10 minutes, and further 60 g of an aqueous 2% by mass calcium chloride solution was dropwise added thereto. In this state, the liquid was taken out in a small quantity as occasion called, and was passed through a microfilter of 2 μm in pore size, where the stirring was continued at 51°C until the filtrate became transparent. After it was made sure that the filtrate became transparent, the product was further stirred for 1 hour. The subsequent procedure of

Example 1 was repeated to produce toner particles 18 to obtain a toner 18.

[0100]<Comparative Example 1>

Water base dispersion 1 of fine resin particles
40.0 g

Water base dispersion of fine colorant particles
10.0 g

Water base dispersion of fine release agent particles
20.0 g

Aqueous 1% by mass calcium chloride solution 20.0 g

Ion-exchanged water 110.0 g

The above components were put to dispersion by using a homogenizer (ULTRATALUX T50, IKA Works, Inc.), and thereafter heated to 45°C in a water bath with stirring by means of a stirring blade. After retention at 45°C for 1 hour, the dispersion obtained was observed on an optical microscope, where it was ascertained that agglomerated particles having an average particle diameter of about 5.5 μm stood formed. Next, 12.1 g of the water base dispersion 9 of fine resin particles was added thereto. In this state, the liquid was taken out in a small quantity as occasion called, and was passed through a microfilter of 2 μm in pore size, where the stirring was continued at 45°C until the filtrate became transparent. After the filtrate became transparent, 40.0 g of an aqueous 5% by mass trisodium citrate solution was added thereto, and thereafter the resultant mixture was heated to 85°C with stirring continued, and this was retained for 120 minutes. Thereafter, the liquid obtained was cooled to 25°C, and thereafter filtered to effect solid-liquid separation, followed by addition of 800 g of ion-exchanged water to the solid matter to carry out stirring and washing for 30 minutes. Thereafter, the solid-liquid separation was again effected. Thus, filtration and washing were repeated until the filtrate came to have an electrical

conductivity of 150 $\mu\text{S}/\text{cm}$, in order to eliminate any influence of a residual surface active agent. The solid matter obtained was dried to obtain toner particles 18. The toner particles 18 had a weight average particle diameter (D_4) of 5.8 μm . In 100 parts of the toner particles thus obtained, 1.8 parts of hydrophobic-treated fine silica powder having a specific surface area of 200 m^2/g as measured by the BET method was mixed by a dry process by means of Henschel mixer (Mitsui Mining & Smelting Co. Ltd.) to obtain a toner 18.

[0101]<Comparative Examples 2 and 3>

Toners 19 and 20 were obtained in the same way as in Comparative Example 1 except that the types and amounts of the water base dispersions were changed as shown in Table 2.

[0102]<Comparative Example 4>

Water base dispersion 1 of fine resin particles	40.0 g
Water base dispersion of fine colorant particles	10.0 g
Water base dispersion of fine release agent particles	20.0 g
Aqueous 1% by mass calcium chloride solution	20.0 g
Ion-exchanged water	110.0 g

The above components were put to dispersion by using a homogenizer (ULTRATALUX T50, IKA Works, Inc.), and thereafter heated to 45°C in a water bath with stirring by means of a stirring blade. After retention at 45°C for 1 hour, the dispersion obtained was observed on an optical microscope, where it was ascertained that agglomerated particles having an average particle diameter of about 6.0 μm stood formed. Then, 40.0 g of an aqueous 5% by mass trisodium citrate solution was added thereto, and thereafter the resultant mixture was heated to 85°C with stirring continued, and this was

retained for 120 minutes to obtain a water base dispersion containing core particles formed of agglomerated particles having been fused. Next, this was cooled to 55°C, and 12.1 g of the water base dispersion 9 of fine resin particles was added thereto, whereupon coarse particles came to form, and hence the production was stopped.

[0103]<Comparative Example 5>

Water base dispersion 1 of fine resin particles
40.0 g

Water base dispersion of fine colorant particles
10.0 g

Water base dispersion of fine release agent particles
20.0 g

Aqueous 1% by mass calcium chloride solution 20.0 g

Ion-exchanged water 110.0 g

The above components were put to dispersion by using a homogenizer (ULTRATALUX T50, IKA Works, Inc.), and thereafter heated to 45°C in a water bath with stirring by means of a stirring blade. After retention at 45°C for 1 hour, the dispersion obtained was observed on an optical scope, where it was ascertained that agglomerated particles having an average particle diameter of about 6.0 μm stood formed. Then, 40.0 g of an aqueous 5% by mass trisodium citrate solution was added thereto, and thereafter the resultant mixture was heated to 85°C with stirring continued, and this was retained for 120 minutes to obtain a water base dispersion containing core particles formed of agglomerated particles having been fused. Next, with stirring continued, water was put into the water bath, where the water base dispersion of core particles was cooled to 25°C. Next, the liquid obtained was filtered to effect solid-liquid separation to obtain a filtrate having a solid matter concentration of 60% by mass. To the filtrate obtained, 12.1 g of the water base

dispersion 9 of fine resin particles was added. Ion-exchanged water was further added thereto, where suspended matter of coarse particles came to form, and hence the production was stopped.

[0104]<Comparative Example 6>

Water base dispersion 1 of fine resin particles	40.0 g
Water base dispersion of fine colorant particles	10.0 g
Water base dispersion of fine release agent particles	20.0 g
Aqueous 1% by mass calcium chloride solution	20.0 g
Ion-exchanged water	110.0 g

The above components were put to dispersion by using a homogenizer (ULTRATALUX T50, IKA Works, Inc.), and thereafter heated to 55°C in a water bath with stirring by means of a stirring blade, whereupon coarse particles came to form, and hence the production was stopped.

[0105]<Comparative Example 7>

Water base dispersion 8 of fine resin particles	82.5 g
Water base dispersion of fine colorant particles	10.0 g
Water base dispersion of fine release agent particles	20.0 g
Aqueous 1% by mass calcium chloride solution	20.0 g
Ion-exchanged water	67.5 g

The above components were put to dispersion by using a homogenizer (ULTRATALUX T50, IKA Works, Inc.), and thereafter heated to 55°C in a water bath with stirring by means of a stirring blade. After retention at 55°C for 20 minutes, the dispersion obtained was observed on an optical microscope, where it was ascertained that agglomerated particles having an average particle diameter of about 6.2 μm stood formed. After addition

of 40.0 g of an aqueous 5% by mass trisodium citrate solution, the resultant mixture was heated to 85°C with stirring continued, and this was retained for 120 minutes to obtain a water base dispersion containing core particles formed of agglomerated particles having been fused. The particle diameter of the core particles was measured to find that their weight average particle diameter (D4) was 6.2 μm .

[0106] Next, with stirring continued, water was put into the water bath, where the water base dispersion of core particles was cooled to 25°C. Next, 11.9 g of the water base dispersion 15 of fine resin particles was added thereto. The subsequent procedure of Example 1 was repeated to produce toner particles 21 to obtain a toner 21.

[0107] Using the above toner particles 1 to 21 and toners 1 to 21, the following evaluation was made. Results obtained are shown in Table 3.

[0108] (Evaluation on How Coarse Particles Have Formed)
Evaluation on how coarse particles have formed was made by the value of number proportion (%) of particles larger than 10 μm in diameter that is found by the analysis of particle size distribution of toner particles.

A: The number proportion of particles larger than 10 μm in diameter is less than 0.5%.

B: The number proportion of particles larger than 10 μm in diameter is from 0.5% or more to less than 1.0%.

C: The number proportion of particles larger than 10 μm in diameter is from 1.0% or more to less than 5.0%.

D: The number proportion of particles larger than 10 μm in diameter is more than 5.0%.

[0109] (Evaluation of Heat-resistant Storage Stability)
The toners were left to stand for 24 hours in a thermostatic chamber having been temperature-controlled to the same temperature as the glass transition point

(Tig) of each first resin, and evaluation was visually made on how far the blocking occurred.

A: Any blocking does not occur.

B: Blocking occurs, but readily disperses upon gentle shaking.

C: Blocking occurs, but disperses upon shaking continued.

D: Blocking occurs, and does not disperse even upon application of force.

[0110] (Evaluation of Fixing Performance)

Each toner and a ferrite carrier (volume average particle diameter: 42 μm) surface-coated with silicone resin were so blended that the toner was in a concentration of 6% by mass to prepare a two-component developer. Using a commercially available full-color copying machine (CLC1100, CANON INC.), unfixed toner images (0.6 mg/cm^2) were formed on an image transfer sheet (64 g/m^2). A fixing unit detached from a commercially available color laser printer (LBP-5500, CANON INC.) was so converted that its fixing temperature was controllable. Using this unit, the fixing of unfixed images was tested. In a normal-temperature and normal-humidity environment (25°C , 40%RH) and setting its process speed at 100 mm/second, the unfixed images were fixed at 9-stage temperatures, stage-wise changing the preset temperature at intervals of 10°C within the range of from 120°C to 220°C . In the fixed images obtained, evaluation was visually made on how offset occurred.

[0111] (Fixing temperature range where any offset does not occur)

A: For 8 stages or more.

B: For 6 stages or more.

C: For 4 stages or more.

D: For 3 stages or less.

Table 2

Example	Toner particles No.	First resin				Second resin				Temperature conditions in steps					
		Type	Amt. (g)	Tig1 (°C)	Teg1 (°C)	Tm (°C)	Type	Amt. (g)	Tig2 (°C)	Teg2 (°C)	Agglomeration step (°C)	Primary fusion step (°C)	Cooling step (°C)	Adhering step (°C)	Secondary fusion step (°C)
1	1	1	40.0	53	58	96	9	12.1	64	70	45	85	25	35	40→65
2	2	1	40.0	53	58	96	9	24.2	64	70	45	85	25	35	40→65
3	3	1	40.0	53	58	96	9	4.0	64	70	45	85	25	35	40→65
4	4	1	40.0	53	58	96	10	12.1	64	70	45	85	25	35	40→65
5	5	1	40.0	53	58	96	11	12.1	64	70	45	85	25	35	40→65
6	6	1	40.0	53	58	96	12	12.1	64	70	45	85	25	35	40→65
7	7	2	40.0	53	59	105	9	12.1	64	70	45	85	25	35	40→65
8	8	3	40.0	51	57	80	9	12.1	64	70	45	85	25	35	40→65
9	9	4	40.0	55	61	115	9	12.1	64	70	45	85	25	35	40→65
10	10	1	40.0	53	58	96	13	12.1	72	78	45	85	25	35	40→65
11	11	1	40.0	53	58	96	14	12.1	58	64	45	85	25	35	40→65
12	12	5	66.6	53	58	96	9	12.1	64	70	45	85	25	35	40→65
13	13	6	40.0	53	58	96	9	12.1	64	70	45	85	25	35	40→65
14	14	7	80.5	53	58	96	9	12.1	64	70	45	85	25	35	40→65
15	15	8	82.5	53	59	100	15	11.9	63	69	45	85	25	35	40→65
16	16	1	40.0	53	58	96	9	12.1	64	70	45	85	45	45	45→65
17	17	1	40.0	53	58	96	16	30.6	64	70	45	85	25	35	40→65
18	18	1	40.0	53	58	96	9	12.1	64	70	45	85	51	51	51→65

Table 2 (cont'd)

Compara- tive Example	Toner parti- cles No.	First resin					Second resin			Temperature conditions in steps					
		Type	Amt. (g)	Tig1 (°C)	Teg1 (°C)	Tm (°C)	Type	Amt. (g)	Tig2 (°C)	Teg2 (°C)	Ag- glom- era- tion step (°C)	Pri- mary fu- sion step (°C)	Cool- ing step (°C)	Ad- her- ing step (°C)	Sec- ondary fusion step (°C)
1	19	1	40. 0	53	58	96	9	12.1	64	70	45	-	-	45	40→65
2	20	1	40. 0	53	58	96	9	24.2	64	70	45	-	-	45	40→65
3	21	1	40. 0	53	58	96	9	28.2	64	70	45	-	-	45	40→65
4	-	1	40. 0	53	58	96	9	12.1	64	70	45	85	55	stop	stop
5	-	1	40. 0	53	58	96	9	12.1	64	70	45	85	25	stop	Stop
6	-	1	40. 0	53	58	96	-	-	-	-	55	stop	stop	stop	Stop
7	22	8	82. 5	53	59	100	15	11.9	63	69	55	85	25	35	40→65

Table 3

	Toner particles D4 (μm)	Toner D4 (μm)	Coarse particles formed	Heat-resistant storage stability	Fixing perform- ance
Example 1	5.9	5.9	A (0.1%)	A	A
Example 2	6.2	6.2	A (0.1%)	A	B
Example 3	5.7	5.7	A (0.1%)	B	A
Example 4	5.8	5.8	A (0.1%)	A	A
Example 5	5.9	5.9	A (0.1%)	B	A
Example 6	6.0	6.0	A (0.2%)	C	A
Example 7	6.0	6.0	A (0.1%)	A	B
Example 8	5.8	5.8	A (0.1%)	A	A
Example 9	5.7	5.7	A (0.1%)	A	C
Example 10	5.9	5.9	A (0.1%)	A	A
Example 11	5.8	5.8	A (0.1%)	C	A
Example 12	6.1	6.1	A (0.1%)	A	A
Example 13	5.7	5.7	A (0.1%)	A	A
Example 14	5.8	5.8	A (0.1%)	B	A
Example 15	6.0	6.0	A (0.1%)	A	B
Example 16	5.9	5.9	A (0.3%)	A	A
Example 17	5.9	5.9	A (0.1%)	B	A
Example 18	6.1	6.1	B (0.8%)	A	A
Comparative Example 1	5.8	5.8	A (0.1%)	D	A
Comparative Example 2	6.2	6.2	A (0.1%)	D	B
Comparative Example 3	6.3	6.3	A (0.1%)	B	D
Comparative Example 4	-	-	D (10.0%)	Unevaluable	Unevaluable
Comparative Example 5	-	-	D (5.9%)	Unevaluable	Unevaluable
Comparative Example 6	-	-	D (7.1%)	Unevaluable	Unevaluable
Comparative Example 7	6.5	6.5	C (4.5%)	B	B

[0112] While the present invention has been described with reference to exemplary embodiments, it is to be understood that the invention is not limited to the disclosed exemplary embodiments. The scope of the following claims is to be accorded the broadest interpretation so as to encompass all such modifications and equivalent structures and functions.

[0113] This application claims the benefit of Japanese Patent

Application No. 2009-188365, filed August 17, 2009,
which is hereby incorporated by reference herein in its
entirety.

CLAIMS

- [1] A process for producing a toner; the process comprising:
- an agglomeration step of mixing at least a water base dispersion of first fine resin particles having a first resin and a water base dispersion of fine colorant particles and, where an extrapolated glass transition onset temperature of the first resin is represented by T_{ig1} and an extrapolated glass transition end temperature thereof by T_{eg1} , agglomerating at a temperature lower than T_{ig1} the first fine resin particles and the fine colorant particles in an aqueous medium by using of an agglomerating agent to form an agglomerate to obtain a water base dispersion of the agglomerate;
 - a primary fusion step of heating the water base dispersion of the agglomerate at a temperature not lower than T_{eg1} to fuse the agglomerate to form core particles to obtain a water base dispersion of core particles;
 - a cooling step of cooling the water base dispersion of core particles to a temperature lower than T_{ig1} to obtain a water base dispersion containing the core particles;
 - an adhering step of mixing, at a temperature lower than T_{ig1} , a water base dispersion of second fine resin particles having a second resin and an agglomerating agent with the water base dispersion containing the core particles to make the second fine resin particles adhere to the core particles to form a shell-adherent substance to obtain a water base dispersion of the shell-adherent substance; and
 - a secondary fusion step of heating the water base dispersion of the shell-adherent substance to a temperature not lower than T_{eg1} to obtain toner particles; and

where an extrapolated glass transition onset temperature of the second resin is represented by T_{ig2} , $T_{ig1} < T_{ig2}$.

- [2] The process for producing a toner according to claim 1, wherein the second resin is in a proportion to the first resin, of from 5% by mass or more to 30% by mass or less.
- [3] The process for producing a toner according to claim 1, wherein the first resin has a softening temperature T_{m1} of from 70°C or more to 110°C or less.
- [4] The process for producing a toner according to claim 1, wherein the second resin has the extrapolated glass transition onset temperature T_{ig2} of from 60°C or more to 80°C or less.
- [5] The process for producing a toner according to claim 1, wherein the second fine resin particles have a volume base median diameter of from 0.05 μm or more to 0.3 μm or less.
- [6] The process for producing a toner according to claim 1, wherein the first resin and the second resin are polyester resin.
- [7] The process for producing a toner according to claim 1, wherein the first fine resin particles are particles in which non-spherical particles having a length/breadth ratio in the range of from 1.5 or more to 10 or less are in a number proportion of 95% by number or more of the whole particles and have an average breadth of from 0.02 μm or more to 1.00 μm or less.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2010/064035

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. G03G9/087 (2006.01) i, G03G9/08 (2006.01) i

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)

Int.Cl. G03G9/087, G03G9/08

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan 1922-1996
 Published unexamined utility model applications of Japan 1971-2010
 Registered utility model specifications of Japan 1996-2010
 Published registered utility model applications of Japan 1994-2010

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	JP 2006-91564 A (Fuji Xerox Co. Ltd) 2006.04.06, 【claim2】 , 【0039】 - 【0042】 , 【0054】 , 【0055】 , 【0069】 , 【0087】 , 【0088】 , 【0093】 , 【0095】 (No Family)	1-7
X	JP 2005-227486 A (Fuji Xerox Co. Ltd) 2005.08.25, 【0040】 , 【0082】 , 【0091】 , 【0092】 , 【0103】 , 【0106】 , 【0118】 , 【0119】 , 【0122】 (No Family)	1-6
X	JP 2008-165177 A (KAO Corporation) 2008.07.17, 【claim1】 - 【claim3】 , 【0014】 , 【0029】 , 【0032】 , 【0040】 , 【0043】 , 【0047】 , 【0053】 , 【0054】 & US 2008/0131804 A1 & DE 102007058288 A & CN 101196702 A	1-6



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

“L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

“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

15.10.2010

Date of mailing of the international search report

09.11.2010

Name and mailing address of the ISA/JP

Japan Patent Office

3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan

Authorized officer

Yuki Fukuda

Telephone No. +81-3-3581-1101 Ext. 3231

2H 4 4 0 6