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(54) ELECTROSTATIC IMAGE-DEVELOPING TONER

(57) The present invention relates to an electrostatic image-developing toner which contains binding resin, a coloring agent, and a releasing agent, as well as to a toner composition and to a method for producing the toner composition. The electrostatic image-developing toner is produced by: (1) a suspension polymerization process (S1) comprising: 1-1) a step of preparing an aqueous dispersion medium; 1-2) a step of dispersing and dissolving a polymerizable monomer mixture; 1-3) a droplet-preparing step of micronizing the liquid prepared in step 1-2) into the liquid prepared in the step 1-1) with high shearing force; and 1-4) a step of radically polymerizing the microparticle liquid droplet prepared in step 1-3); (2) a seeded polymerization process (S2) comprising: 2-1) a step of dissolving and dispersing the releasing agent; and 2-2) a step of the seeded polymerization of the liquid prepared in step 2-1); (3) a process in which particles produced in the suspension polymerization process (S1) and in the seeded polymerization process (S2) agglomerate; (4) a process of fusing the particles agglomerated in process (3) by means of heat; (5) a process of cleaning and drying the toner produced in the process (4); and (6) a process of adding an agent for providing the toner produced in the process (5) with electrostatic properties and flowability.

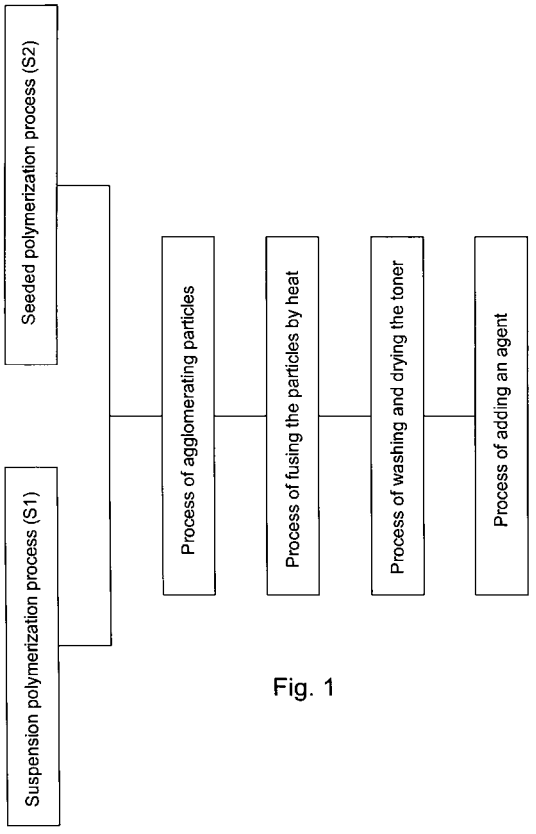

Fig. 1

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Description

Technical Field

[0001] The present invention relates to, in the toner including a binding resin, a coloring agent and a releasing agent, an electrostatic image developing toner, its composition, and a preparation method thereof. The electrostatic image developing toner is prepared by the method comprising:

(1) a suspension polymerization process(S1) comprising:

1-1) a step of preparing a water-borne dispersion medium,
1-2) a step of dispersing and dissolving a polymerizable monomer mixture,
1-3) a liquid droplet-preparing step of micronizing the liquid prepared in the step 1-2) into the liquid prepared in the step 1-1) with high shearing force, and
1-4) a step of radically polymerizing the fine particle liquid droplet prepared in the step 1-3);

(2) a seeded polymerization process(S2) comprising:

2-1) a step of dissolving and dispersing the releasing agent, and
2-2) a step of the seeded polymerization of the liquid prepared in the step 2-1);

(3) a process of agglomerating particles produced in the suspension polymerization process(S1) and in the seeded polymerization process(S2);
(4) a process of fusing the particles agglomerated in the process(3) by heat;
(5) a process of washing and drying the toner produced in the process(4); and
(6) a process of adding an agent for providing the toner produced in the process (5) with electrostatic properties and fluidity.

[0002] The toner prepared according to the method of the present invention has a narrow particle size distribution, has small consumption and imagery stability with high definition.

BACKGROUND ART

[0003] Recently, the use of an image development machine such as an electro photography copy machine and printer is expanded, particularly digital image scan devices are generally propagated and documents having high quality images and excellent expressiveness are needed, also faultlessness and, moreover, a high quality of printed images are required by supplying and growth of presentation software.

[0004] Prior various electro photographic methods are disclosed at US Patent 2297691 and Japanese Patent 1968-23910 (US Patent 3666363) and so on.

[0005] Generally, a copy image or a printed image may be obtained by forming an electrostatic latent image on a photosensitive member by various means using photoconductive materials, developing the latent image using a toner and transferring the toner image to a transfer medium such as a paper as occasion demands, and fixing thereof by action of heat, pressure, heat and pressure, or solvent steam. Also, the abovementioned processes are repeated after cleaning the toner left on the photosensitive member without transfer using various means.

[0006] Various methods such as the method for developing an electrostatic image using a toner or the method for fixing a toner image are conventionally provided. The toner used for these purposes is generally a grinding toner made as a toner having a desired particle diameter obtained by fusing and mixing a coloring agent consist of a dye or a pigment of thermoplastics and uniformly dispersing thereof, and grinding finely and sorting thereof.

[0007] However, while the toner made by the abovementioned method has a good quality, it has some problems in view of imagery quality. For example, the resin composition in which the coloring agent is dispersed is easily breakable enough to be finely grinded by an economical manufacturing device. However, the resin composition is easy to form particles having a wide particle diameter substantially in fine grinding rapidly, particularly may cause a seriously problem such as document pollution because there are relatively small particles thereof. In this context, while a sorting process is performed in order to remove undesired particles, there is, in this case, a critical problem that it causes high production costs that production yield in manufacturing is low because of wide particle size distribution.

[0008] Meanwhile, to solve the problem of the toner made by the grinding methods, Japanese Patent 1962-10231, 1968-10799, 1978-14895 provide the methods for product a toner by suspension polymerization. In the suspension polymerization method, toner particles having a desired particle diameter are obtained by forming monomer composition

by uniformly dissolving and dispersing polymerizable monomer, a coloring agent, polymerization starter, if required, cross-linker, charge control agents, and other addition agents, dispersing the monomer composition to aqueous-phase medium including dispersion stabilizer. The method has some advantages that it needs not the breakable property of the resin composition because of having not the grinding step, and can use soft materials, and also that the toner particles has uniform frictional electrification because the a coloring agent does not expose to the surface of the toner particles. Also, the method is very effective in the view of cost reduction such as energy save, production time shortening, process yield improvement, etc. because the sorting step can be omitted.

[0009] However, if the particle diameter of the toner is finer even in the case of using the method, the coloring agent come easily out the surface of the toner particles so that the performance of the toner will be negatively influenced. Consequently, the method has a disadvantage that the uniform electrification may be degraded and the development capability of the toner may be changed.

[0010] The phenomenon is noticeable in case of copy or printing particularly in environment of high temperature and humidity. In relation to that, the method for spreading a resin on the surface layer of the toner particles such as described in Japanese Patent 1988-73277, 1992-35662 is suggested. Though the method may prevent the abovementioned phenomenon affected by a coloring agent by making the thick of the spread layer be thicker, it has a serious problem that absolute value of the quantity of electron charge become smaller because the toner contains little composition having charge controllability. Such problem is being recognized and reported substantially in many case.

[0011] To solve the problem, the method for adhering charge control agents to the surface of the toner such as described in Japanese Patent 1990-62666, 1990-630635, 1987-273558, and 1994-134437 is suggested. However, the method may cause a serious problem in operation as, in case of repeat of copy or printing, the charge control agents are separated from the surface of the toner particles in view of durability of the toner.

[0012] Meanwhile, Japanese Patent1986-238846, and 1994-197203 disclose the use of an electrostatic image developing toner containing the toner particles made by suspension polymerization method which performs dispersing polymerizable monomer composition containing polyester resin to water-borne medium and assembling thereof. However, it is expected to provide an electrostatic image developing toner having a better friction electrification, multiple operation, heat-resisting offset property and translucency.

DISCLOSURE OF INVENTION

Technical purpose of the invention

[0013] Improvement of low temperature fixing property is an important factor for performing high speed processing and full color printing by a printer and a copy machine. In this respect, it is preferable a toner obtained by a polymerization method wherein obtainment of toner particles of which the particle diameter has a sharp distribution and is very small may be relatively easy. It is essential that the toner used in a full color copy machine or a full color printer endures well a compound color in fixing step, thus, improvement of color reproduction or maintenance of transparency of OHP image is very important. Also, it is preferable that the color toner is made with the resin having better fusing property and lower molecular weight than a black-and-white toner.

[0014] Wax having relatively high degree of crystallization, for example, polyethylene wax and polypropylene wax are used as releasing agents of the black-and-white toner in order to improve heat-resisting offset property in fixing. However, in the case of the full color toner, because of high degree crystallization of the wax, transparency of image lowers in printing through OHP and serious problems occurs in high speed processing and low temperature fixing property.

[0015] Therefore, generally wax having a low degree of crystallization and a low melting point should be added in order to improve the low temperature fixing property.

[0016] Thus, for a toner, particularly a color toner made by a polymerization method, it is required to provide a toner which is solvable smoothly the problems occurred all in development and fixing property.

Technical solution

[0017] The object of the present invention is to provide an electrostatic image developing toner which solves the abovementioned problems, a composition of the toner and a preparation method of the composition. The present invention relates to the electrostatic image developing toner which is prepared by the following method, and the preparation method comprising:

(1) a suspension polymerization process(S1) comprising:

1-1) a step of preparing an water-borne dispersion medium,
1-2) a step of dispersing and dissolving a polymerizable monomer mixture,

1-3) a liquid droplet-preparing step of micronizing the liquid prepared in the step 1-2) into the liquid prepared in the step 1-1) with high shearing force, and
1-4) a step of radically polymerizing the fine particle liquid droplet prepared in the step 1-3);

(2) a seeded polymerization process(S2) comprising:

2-1) a step of dissolving and dispersing the releasing agent, and
2-2) a step of the seeded polymerization of the liquid prepared in the step 2-1);

(3) a process of agglomerating particles produced in the suspension polymerization process(S1) and in the seeded polymerization process(S2);
(4) a process of fusing the particles agglomerated in the process(3) by heat;
(5) a process of washing and drying the toner produced in the process(4); and
(6) a process of adding an agent for providing the toner produced in the process (5) with electrostatic properties and fluidity.

[0018] The other object of the present invention is to provide a method to prepare a toner having a narrow particle size distribution, small consumption and good imagery stability with high definition.

[0019] The coloring agent used in the present invention is preferably selected from known pigments which may be used in the toner and are used.

[0020] For example, there are black pigment, yellow pigment, magenta pigment, cyan pigment as the pigments, and there are carbon black, aniline black, nonmagnetic ferrite, and magnetite etc, as the black pigment.

[0021] The carbon black for black pigment exists as an aggregate of very fine first particle, and is easy to be coarsened because of re-aggregation in being dispersed as pigment dispersion agent. A degree of re-aggregation of the carbon black particles has relevance to a large/small quantity of impurities contained in the carbon black, therefore it is very preferable that the quantity of impurities is contained to the extent that the polymerization is not prevented. In the present invention, it is preferable that the carbon black is made by Furnace method.

[0022] A compound which represents Nitrogenous fused compound, Isoindolinone compound, Azo metal complex compound, Arylamine compound, etc. is used as the yellow pigments. Concretely, C.I. Pigment Yellow 12, 13, 14, 15, 17, 62, 74, 83, 94, 95, 109, 110, 111, 128, 147, 150, 155, 168, 180, 194, etc. are used, and it is able even to use only one or mixed more than one of the Yellow Pigments for color mixture.

[0023] Nitrogenous fused compound, Pyrrole compound, Anthraquinone, Quinacridone compound, Naphthol compound, Benzoimidazolone compound, Thio indigo compound, Perylene compound are used as the magenta pigment. Concretely, C.I. Pigment Red 2, 3, 5, 6, 7, 23, 48:2, 48:3, 48:4, 57:1, 81:1, 122, 144, 166, 169, 173, 184, 185, 202, 206, 207, 209, 220, 221, 238, 254, C.I. Violet 19 etc. are preferable. Among them, Quinacridoneseries Pigment represented by C.I. Pigment Red 122,202,207,209, C.I. Pigment Violet 19 is more preferable. C.I. Pigment Red 122 of the Quinacridoneseries Pigment is very preferable.

[0024] Copper phthalocyanine compound and its derivatives, Anthraquinone compound etc. may be used as the cyan pigment. Concretely, C.I. Pigment Blue 1, 15, 15:1, 15:2, 15:3, 15:4, 60, 62, 66 etc. and C.I. Pigment Green 7,36 etc. may be used particularly.

[0025] Such a coloring agent may be used alone, in a mixture or in a solid solution. The coloring agent is suitably selected considering color, a degree of color saturation, brightness, weathering, OHP transparency, and dispersion property in the toner particles.

[0026] The coloring agent may be added by 1 to 20 parts by weight based on 100 parts by weight of a bonding agent.

[0027] In the present invention, the toner particles should be used with attention of a unique polymerizing inhibitory action or an aqueous phases transfer property contained in the coloring agent because it is made by polymerization method. Surface of the coloring agent may be modified by hydrophobic treatment using materials without polymerization inhibitory property. Particularly, the carbon black has polymerization inhibitory property, thus it should be careful to use it.

[0028] In the method for manufacturing toner particles, it is preferable to add a polymer or copolymer having polar group (hereafter referred as polar resins) and polymerize thereof, add a polar monomer and polymerize thereof, or mixed-add the polar resins and the polar monomer and polymerize thereof before manufacturing fine particles of suspension polymerization process.

[0029] The polymer and copolymer having polar group which may be used in the present invention are followed.

[0030] For example, it is nitrogen-containing polymer such as ethyl of methacrylic dimethyl acid network, ethyl of metacrylic acid diethyl network, etc. or copolymer with styrene-unsaturated carbonic acid ester, etc. or nitrile-based monomer such as acrylonitrile, halogen-containing based monomer such as vinyl chloride, unsaturated carbonic acid such as acrylic acid or methacrylic acid etc. or a polymer such as unsaturated diacid, unsaturated diacid anhydride, nitrogen-containing monomer, etc. or copolymer with styrene-based monomer, etc. or polyester resins, or epoxy resins.

Among them, the polyester resins are very preferable.

[0031] Further, the monomers having polar group which may be used in the present invention are as follows.

[0032] The monomers having polar group are divided into acidic monomer and basic monomer. The acidic monomer is a polymerizable monomer having carboxyl group such as acrylic acid, methacrylic acid, itconic acid, maleic acid, fumaric acid, cinnamic acid, etc. or a polymerizable monomer having sulfonic acid group such as sulfonated styrene, etc. or a polymerizable monomer having sulfonamide group such as vinyl benzene sulfonamide, etc. also, the basic monomer is a nitrogen-containing heterocyclic polymerizable monomer such as aromatic vinyl compounds, vinyl pyridine, vinyl pyrrolidone etc. which have amino group such as styrene network.

[0033] Such polar monomer may be used alone, or used in mixture. Also, it is possible that the polar monomer exists as salts with counter-ions. Among them, it is preferable to use the acidic monomer, more preferable to use acrylic acid or methacrylic acid.

[0034] It is preferable that a ratio of an amount of the polar resins or the polar monomer or the mixture of the polar resins and the polar monomer in total amount of 100% by weight of polymerizable monomer consisting of binder resins as fine particles of suspension polymerization process or seeded polymerization process is an amount of 0.05% by weight to 20% by weight, more preferable 0.5% to 15% by weight. In the case that the raio is within the range, the fine particles of suspension polymerization process and seeded polymerization process to be gotten have improved stability is easy for a shape or a particle diameter of the particles to be controlled. However, in the case of less than 0.05% by weight of the ratio, the polymerizable monomer exists as a mixed layer, thus it is easy for assembly and polymerization stability to be deteriorated, also it causes the hardness of the generated resins particles surface layer to lower and properties of charge stability, durability, conservativeness, etc. as a toner to lower. Also, in the case of exceeding 20% by weight of the ratio, viscosity of the generated polimerizable monomer is too increased, therefore it is difficult to control the particle diameter of the desired assembling particles, and also cause the toner particles not to fuse and fixing property to damage seriously.

[0035] Polymerizable monomers having polar group which may be used in the present invention are followed. For example, there are styrene monomers such as styrene, chlorostyrene, dichlorostyrene, p-tert-butyl styrene, p-n-butyl styrene etc., acrylic acid ester monomers such as acrylic acid methyl, acrylic acid ethyl, acrylic acid propyl, acrylic acid n-butyl, acrylic acid iso butyl, acrylic acid hydrixy ethyl, acrylic acid ethylhexyl, etc., methacrylic acid ester monomers such as methacrylic acid methyl, methacrylic acid ethyl, methacrylic acid propyl, methacrylic acid n-butyl, methacrylic acid iso butyl, methacrylic acid hydroxyl ethyl, methacrylic acid ethylhexyl etc., acrylamid monomers such as acrylamid N-propyl, acrylamid N,N-dimethyl, acrylamid N,N-dipropyl, acrylamid N,N-dibutyl, etc., monomers such as acrylo nitrile, methacrylonitryl etc. While such polymerizable monomers are used alone or in mixture, it is preferable to use a styrene monomer or the styrene monomer with one monomer or more than one monomer selected from acrylic acid ester monomers and methacrylic acid ester monomers in order to obtain good toner particles in a view of developing property and durability etc, in developing.

[0036] Also, the polymerizable monomers are generally used alone or appropriately with mixture for theoretical Glass Transition Temperature(Tg) to be 40~75°**C** which is disclosed at Polymer Handbook second edition III pp.139~192(Jone Wiley & sons private). In the case of less than 40°**C** of the theoretical Glass Transition Temperature(Tg), it is easy to encounter some problems related to preserving stability and durable stability of the toner, and in the case of exceeding 75°**C**, fixing point of the toner become high. Particularly, in the case of a color toner in order to form full color image, it is not preferable because, in fixing, mixing color property is declined, color reproducibility is feeble, and also transparency of OHP image is lower.

[0037] In the method for manufacturing toner particles according to the present invention, it is one preferable type to add releasing agents as seeds and performing seeded polymerization when preparing seeded polymerization process particles. When the releasing agents are being exposed on the toner surface, toners are easy to be agglomerated each other, and the toners may be fixed to a photo conductor when printing. However, according to the present invention, the releasing agents are not exposed on the toner surface after agglomeration and large amount of wax can be used by containing the agent by seeded polymerization, and it may manufacture toner particles having high resolution and anti-offset property and also suitable to image forming device.

[0038] Usable wax as a releasing agent used in the present invention is petroleum-based wax and its derivatives such as paraffin wax or styrene modified paraffin wax, micro crystal wax, petrolatum, montan-based wax and its derivatives, hydrocarbon wax and its derivatives by Fischer-Tropsch method, polyolefin wax and its derivatives represented by polyethylene, and natural wax and its derivatives such as carnauba wax, candelila wax, etc., and the derivatives contain block copolymer with oxide or vinyl-based monomer, and modified graft monomer. Also, fatty acids or compounds thereof such as higher aliphatic alcohol, stearate, palmitic acid, etc., acid amides wax, ester wax, plant-based wax, animal-based wax, etc. may be used.

[0039] In a curve measured by DSC(Differential Scanning Calorimetry), it is preferable that such wax component has a maximum heat absorption peak at 40°C to 110°C in heat up. It has a big efficiency of low temperature deposition and also shows an effective releasing property to have the maximum heat absorption peak in the temperature range. It is

not preferable to exceed 110°**C** of the maximum heat absorption peak because the fixing temperature is climbing and low temperature offset is generated. For example, DSC 200F3 of NETZSCH is used for measuring the maximum heat absorption peak of the wax component. Fusing point of indium and zinc is used for temperature correction of a detection part of the device, and the heat of fusion of indium is used for calorie correction. Sample for the measurement is aluminum cell, and the measurement is performed at 10**°C**/minute of heat up rate.

[0040] It is preferable that a content of the wax component as the releasing agent is an amount of 0.1 to 30% by weight, more preferable 0.5% to 20% by weight. Being less than 0.1% by weight of the content, it causes a releasing property to lower, so enough low temperature offset inhibitory effect is not shown. In case of exceeding 30% by weight, dispersion property of other material is deteriorated, or an aggravation of toner fluidity or a falling-off in image property is caused.

[0041] In the present invention, charge control agent may be used in order to stabilize charge property of toner particles. What is known as the charge control agent may be used, particularly it is preferable to use a charge control agent which may have a rapid charging rate and keep stably uniform charging quantity. Also, it is preferable that the charge control agent has a low polymerizable inhibition and has not any solubilized material to water-borne dispersion medium. Concretely, as the charge control agent, metal compounds of aromatic series carboxylic acids such as salicylic acid, alkyl salicylic acid, dialkyl salicylic acid, naphthoeic acid, dicarboxylic acid, metallic salt or metal complex of azo dye or azo pigment, polymer compound having sulfonic acid or carboxyl acid in a branch, boron compounds, urea compounds, silicon compounds, carixareum, etc. are used as negative charge control agents, and nigrosine-based compounds, quaternary ammonium salts, polymer compounds having the quaternary ammonium salts in a branch, guanidine compounds, imidazole compounds, etc. are used as positive charge control agents.

[0042] It is preferable to use the charge control agent with 0.5 to 10 parts by weight for 100 parts by weight of polymerizable monomer. However, in the present invention, it is not essential to use charge control agent. Thus, in the developing device of the image forming machine, charging quantity or charging rate may be controlled by actively using absence of restriction of layer pressure of the toner or frictional charging with developer bearing body(the abovementioned rotational sleeve). In the case of adding the charge control agent, it is preferable to determine its quantity to be added in view of using type of toner particles to be obtained.

[0043] In the present invention, it is possible to use with a known emulsifier, or organic and inorganic dispersion agent as dispersion stabilizer in combination.

[0044] The emulsifier used as an aqueous dispersion stabilizer may be any of known emulsifiers, and it may be one or more than one surfactants in combination selected from a group consisting of cationic surfactant, anionic surfactant and non-ionic surfactant.

[0045] The cationic surfactant may be, for example, dodecyl ammonium chloride, dodecyl ammonium bromide, dodecyl trimethyl ammonium bromide, dodecyl pyridium chloride, dodecyl pyridium bromide, hexadecyl trimethyl ammonium bromide and the like.

[0046] The anionic surfactant may be, for example, fatty acid salt such as sodium stearate, sodium dodecanate and the like, sodium dodecyl sulfate, sodium dodecyl benzenesulfonate, sodium lauryl lactate and the like.

[0047] The non-ionic surfactant may be, for example, polyoxyethylene dodecyl ether, polyoxyethylene hexadecyl ether, polyoxyethylene nonyl phenyl ether, polyoxyethylene lauryl ether, polyoxyethylene sorbitant ether and the like.

[0048] The amount of the emulsifier may be commonly 1 to 20 parts by weight for 100 parts by weight of the polymerizable monomer, preferably, and as a protecting colloid, one or more than one in combination selected from the group consisting of polyvinyl alcohols such as partly or completely safonified polyvinyl alcohol, cellulose derivatives such as hydroxyl ethyl cellulose, inorganic dispersing agent such as magnesium phosphate, magnesium hydrogen phosphate, magnesium dihydrogen phosphate, aluminum phosphate, zinc phosphate, calcium phosphate tribasic, calcium hydrogen phosphate, calcium dihydrogen phosphate, and the like may be added to the emulsifier.

[0049] For producing toner particles, the toner particles may be produced by using polymerization reaction.

[0050] For example, there are suspension polymerization method, emulsion polymerization method, emulsion associative polymerization method, dispersion polymerization method, suspension aggregation polymerization method, etc. In the present invention, a mixture except the releasing agent is process by suspension polymerization process to prepare fine particles, and the releasing agent is processed by seeded polymerization process to prepare fine particles, and then each fine particles are agglomerated into a desired size and fused by heat. The suspension seeded aggregation polymerization method is particularly preferred in view of degree of freedom of particle design and ease of control of particle size.

[0051] In the method for preparing the toner particles of the present invention, first of all, a mixture except the releasing agent is process by suspension toner process to prepare fine particles, and separately, the releasing agent is processed by seeded polymerization process to prepare fine particles, and then each toner particle suspension and seeded polymerization particle suspension are mixed and agglomerated into a desired size and fused by heat, preferably.

[0052] In the method for preparing fine particles of the present invention by suspension polymerization process(S1), the fine particles polymerized by suspension polymerization process are produced by dispersing at least one selected from the group consisting of polymerizable monomers, polar resins, coloring agents except releasing agent in an water-

borne dispersion medium mixed with one or a mixture of more than one selected from emulsifier, and organic and inorganic dispersion stabilizer, producing liquid droplet particles of polymerizable monomer composition, adding polymerization starter into the mixture before polymerization, adding thereof to the liquid droplet particles, and polymerizing polymerizable monomer components, and in the method for preparing fine particles by seeded polymerization process (S2), the seeded polymerization fine particles containing wax are produced by dispersing the releasing agent in an water-borne dispersion medium containing the emulsifier in advance and adding the releasing agent as a seed followed by polymerizing thereof using monomers for seeded polymerization.

[0053] Toner particles having good degree of freedom of particle design and very uniform particle size distribution can be obtained by mixing the fine particle suspension prepared by suspension polymerization process and the fine particle suspension prepared by seeded polymerization process and agglomerating thereof using an agglomerating agent into a desired size, and then fusing thereof by heat. Because surface and shape of obtained toner particles are uniform and the releasing agents are not exposed on the surface, charging property and cohesion thereof are good, and good developing property is represented in electrostatic latent image developing in the electric photo process.

[0054] In the method for producing micron by suspension polymerization process of the present invention, polymerizable monomer mixture which is solved uniformly or dispersed using a homogenizer such as homogenizer, ball mill, colloid mill, ultrasonic homogenizer, etc. is suspended in the water-borne medium. At this time, using high speed homogenizer such as high speed blender or ultrasonic homogenizer, the polymerizable monomer mixture is stabilized by keeping the fine particle in the water borne medium in liquid droplet state in order to disperse uniformly the polymerizable monomer mixture in the water-borne dispersion medium.

[0055] Polymerizable monomer droplets in stabilized fine particle state are polymerized with a polymerization starter. At this time, while the temperature of polymerization is determined according to properties of matter of the polymerization starter, particularly a half-life temperature, the temperature is set at more than 40°C, generally 50 to 90°C and the polymerization is started.

[0056] It is preferable to use a water-soluble starter and an oil-soluble starter as the polymerization starter, wherein the half-life of the oil-soluble starter is 0.5 to 30 hours in polymerization reaction. For example, persulfates such as peroxide, potassium persulfate, etc., organic peroxides such as benzoylperoxide, lauryl peroxide, etc., azo-group compounds such as 2,2'-azobis isobuthyronitrile, 2,2'-azobis(2,4-dimethylvaleronitile), etc., redox-group starter, etc. are used. Particularly, azo-group compounds or organic peroxides are preferable.

[0057] In such polymerization starter, it is possible to obtain a polymer having a maximum in the range of weight average molecular weight 10,000 to 300,000 using quantity of 0.1 to 20 parts by weight of alone or more than one of polymerization starter for 100 parts by weight of polymerizable monomer, and to give preferable strength and proper fusing property to toner particles. Departing the half-life and addition quantity of the polymerization starter from the range, polymerizable monomers are not polymerized enough, or a good property of matter of the polymerized binding resins may have damage.

[0058] The abovementioned polymerization starter may be added to the polymer whenever before adding the polymerizable monomer, simultaneously adding it, or after adding it, and such adding methods are performed with combined as demanded.

[0059] Also, in the present invention, a cross-linker may be added, and preferable adding quantity thereof is 0.001 to 15% by weight for 100 parts by weight of polymerizable monomer. Generally two more polymerizable compounds having a double band are used as the cross-linker. For example, aromatic series divinyl compound such as divinylbenzen, divinylnaphthalene, etc., carboxylic acid ester having two double bands such as ethyleneglycole, diacrylate, ethyleneglycoledimethacrylate, 1,3-buthandioldimethacrylate, etc., compounds having three more vinyl groups such as divinyl aniline, divinyl ester, divinyl sulfide, divinyl sulfone, and divinyl compounds are used alone or with mixed. The adding quantity of the cross-linker being less than the range, it does not work enough. However, exceeding the range, the property of matter of binding resins may have bad influence.

[0060] Also, polymerization time being determined in view of polymerization conversion ratio, it is preferable that it is more than 30 minutes, generally 1 hour to 20 hours.

[0061] Further, in the method for producing fine particles by seeded polymerization process of the present invention, the releasing agents can be mixed by uniformly dissolving or dispersing the releasing agent using a homogenizer such as high speed homogenizer, ball mill, colloid mill, ultrasonic homogenizer, etc. in the water-borne medium. At this time, the releasing agent dispersion is stabilized by keeping the fine particles in the water-borne.

[0062] The releasing agent dispersions in stabilized fine particle state are polymerized with polymerization monomer and a polymerization starter. At this time, the temperature of polymerization is determined according to properties of matter of the polymerization starter, and the temperature is set at more than 40°C, generally 50 to 95°C and the polymerization is started.

[0063] It is preferable to use a water-soluble starter and an oil-soluble starter as the polymerization starter, wherein the half-life of the oil-soluble starter is 0.5 to 30 hours in polymerization reaction. For example, persulfates such as peroxide, potassium persulfate, etc., organic peroxides such as benzoylperoxide, lauryl peroxide, etc., azo-group com-

pounds such as 2,2'-azobis isobuthyronitrile, 2,2'-azobis(2,4-dimethylvaleronitile), etc., redox-group starter, etc. are used. Particularly, organic peroxides or azo-group compounds are preferable.

[0064] In such polymerization starter, it is possible to obtain a polymer having a maximum in the range of weight average molecular weight 10,000 to 300,000 using quantity of 0.1 to 20 parts by weight of alone or more than one of polymerization starter for 100 parts by weight of polymerizable monomer, and to give preferable strength and proper fusing property to toner particles. Departing addition quantity of the polymerization starter from the range, polymerizable monomers are not polymerized enough, or a good property of matter of the polymerized binding resins may have damage.

[0065] The abovementioned polymerization starter may be added to the polymer whenever before adding the polymerizable monomer, simultaneously adding it, or after adding it, and such adding methods are performed with combined as demanded.

[0066] Also, in the present invention, a cross-linker may be added, and preferable adding quantity thereof is 0.001 to 15% by weight for 100 parts by weight of polymerizable monomer. Generally two more polymerizable compounds having a double bond are used as the cross-linker. For example, aromatic divinyl compound such as divinylbenzen, divinylnaphthalene, etc., carboxylic acid ester having two double bonds such as ethyleneglycole, diacrylate, ethyleneglycoledimethacrylate, 1,3-buthandioldimethacrylate, etc., compounds having three more vinyl groups such as divinyl aniline, divinyl ester, divinyl sulfide, divinyl sulfone, and divinyl compounds are used alone or with mixed. The adding quantity of the cross-linker being less than the range, it does not work enough. However, exceeding the range, the property of matter of binding resins may have bad influence.

[0067] Also, polymerization time being determined in view of polymerization conversion ratio, it is preferable that it is more than 30 minutes, generally 1 hour to 30 hours.

[0068] The average particle diameter(D50) of the fine particles prepared by suspension polymerization process and seeded polymerization process may be 50 nm to 10 μ**m**, and preferably, 100 nm to 5 μ**m.**

[0069] In the case that the average particle diameter(D50) of the fine particles prepared by suspension polymerization process and seeded polymerization process is less than 50 nm, there are some difficulties that much aggregation agents are needed, and also much fine particles may be contained. Meanwhile, in the case that it exceeds 10 μ**m**, there is a problem that the size of the particles after aggregation is too coarse so that the particles are scattered and a resolution is lowered in electrophotographic process, thereby final image has a bad influence.

[0070] The dispersion of the fine particles prepared by suspension polymerization process and the dispersion of the fine particles prepared by seeded polymerization process produced by the polymerization are mixed and gone through aggregation process using a proper aggregation agent to have a desired particle diameter.

[0071] An aggregation treatment used in the aggregation process is generally a method for heating in a blender, a method for adding an electrolyte, and a method combined thereof, etc.

[0072] In the case of the method for adding an electrolyte of the aggregation treatments, it is preferable that the electrolyte is any one of organic material or inorganic material. Concretely, it is an inorganic salts having monovalent metallic cations such as NaCl, KCl, LiCl, Na_2SO_4, K_2SO_4, Li_2SO_4, CH_3COONa, $C_6H_5SO_3Na$, etc., an inorganic salts having divalent metallic cations such as $MgCl_2$, $CaCl_2$, $MgSO_4$, $CaSO_4$, $ZnSO_4$, etc., an inorganic salts having trivalent metallic cations such as $Al_2(SO_4)_3$, $Fe_2(SO_4)_3$, etc. It is preferable to use inorganic salts having multivalent metallic cations in view of a high speed and high yield. Also, it is preferable to use the inorganic salts having monovalent metallic cations in view of controlling the speed of aggregation growth. What is used as the electrolyte may control an aggregation property by using one selected of inorganic salts having monovalent, divalent, trivalent metallic cations or with mixed thereof. Particularly, it is very preferable to select properly one of inorganic salts having divalent or trivalent metallic cations so that the aggregation property of the particles has a high speed, and then to select inorganic salts having monovalent metallic cations so as to control the aggregation speed.

[0073] Also, it is preferable to adding the electrolytes not at the same time but slowly in intermittent or continuous method. While the adding time is different according to a kind of the electrolytes and quantity to be used thereof, it is preferable for addition to be carried out during one more minutes. Generally, when the electrolytes being put at the same time, it is difficult to control the aggregation of the particles because the aggregation starts suddenly. Also, a desired toner particles and particle diameter distribution cannot be obtained because there remain many fine particles or too many aggregates.

[0074] Also, in the case of carrying out the aggregation with adding the electrolytes, it is preferable that temperature of the aggregation process is 0°C to 90°C, more preferably 5°C to 80°C. To control the temperature of the aggregation process is one method for control the particle diameter and shape of special range of the present invention. It is possible for the aggregation process to be carried out by controlling pH or by adding polar organic solution such as alcohol.

[0075] In the present invention, it is preferable that fusing process temperature by heat is preferably more than glass transfer temperature(Tg) of first suspension toner particles in micron state, more preferable is more Tg+5°C and less than Tg+50°C. Also, while time needed in the fusing process is different according to the shape of toner, it is preferable that it is generally 0.1 to 20 hours after arriving at more glass transfer temperature of fine particles prepared by suspension polymerization process and seeded polymerization process. It is more preferable to be kept during 0.5 to 15 hours.

[0076] As such, fine particles prepared by suspension polymerization process and seeded polymerization process are fused and integrated by heat. While particle aggregates before fusing process are aggregate by electrostatic or physical aggregation, various types of toner such as the shape for toner particles to be aggregated, for example, a potato type or sphere type may be obtained by controlling temperature and time, etc. of fusing process through the fusing process.

[0077] The toner aggregate gone through each abovementioned processes is sorted into solid/ liquid according to a known method, and a desired toner particles may be obtained by collecting the particle aggregate, washing and drying thereof as demanded.

[0078] Surface of the desired toner particles obtained by the abovementioned processes is mixed to with a known additive in order to control fluidity or developing property. The additive is metal oxide such as alumina, silica, titanium dioxide, zinc oxide, zirconium oxide, cesium oxide, talcum, hydrotalcite, etc., metal titanate such as hydroxide, calcium titanate, strontium titanate, barium titanate, etc., nitride such as titanium nitride, silicon nitride, etc., acrylic carbide based resins such as titanium carbide, silicon carbide, etc., organic particles such as melamine resins, and the mixture thereof. Silica, titanium dioxide, alumina among them is preferable. Also, for example, the surface is more preferable to be treated by silane coupling agent or silicon oil, and so on. It is preferable that average first particle diameter is in range of 500 nm, more preferable 5 to 100 nm. Also, in the range, an additive having the small particle diameter and an additive having the large particle diameter are preferable to be used together.

[0079] Total mixed quantity of the additive is preferable to be in range of 0.05 to 10 parts by weight for 100 parts by weight of the toner particles, more preferable 0.1 to 5 parts by weight.

[0080] The toner of the present invention obtained by the abovementioned methods is for distribution of charging quantity to be sharp in comparison to prior toner. The distribution of charging quantity is related to particle diameter of toner and position of charge control agent. Thus, in the case of wide distribution of the particle diameter as prior toner, charging quantity became wide. Thereby, the wide distribution of charging quantity makes it difficult to control with a desired developing condition, makes the ratio of low charging particles of high charging particles increase, and thus results in various image faults.

Effects of the invention

[0081] The present invention is easy to control particle diameter and rounded image by producing particles by processing a mixture except the releasing agent by suspension polymerization process to prepare fine particles, and by producing particles by separately processing the releasing agent by seeded polymerization process followed by mixing and agglomerating the suspension polymerization particle suspension and the seeded polymerization particle suspension into a desired size, and fusing thereof by heat. Also, the present invention provides an electrostatic image developing toner having uniform distribution of particle size in comparison to prior toner producing processes and, thus its toner consumption is low and is useful to an electro photographic process requiring high resolution.

BRIEF DESCRIPTION OF DRAWINGS

[0082]

Fig. 1 shows preparing process according to embodiment of the present invention.

DESCRIPTION OF SPECIFIC EMBODIMENTS

[0083] Now, various embodiments of the present invention will be specifically described. However, the embodiments not are intended to limit the scope of the present invention.

[0084] In the following examples, "part" is represented as "part by weight".

[Preparation Example 1] Preparation of Black Pigment Fine particle by Suspension Polymerization Process

o Preparation of water-borne dispersion medium

[0085] Anionic surfactant SDBS(Sodium Dodecyl Benzene Sulfonate) 20% aqueous solution 0.1 part and ion-exchanged water 300 parts were added to a stirrer, a heat-cooling device, a reflux device and a detachable reactor abled to insert each raw material (volume: 2 L), and stirred using TK type homomixer Mark (made by Primix) at 5,000 RPM in the condition of heating to 60°**C** under nitrogen gas flow to obtain water-borne dispersion medium.

o Polymerizable monomer mixture dispersion and solution process

[0086]

Styrene 80 parts
n-butyl acrylate 20 parts
Carbon black(first particle diameter 31nm) 5 parts
Polar resins(Polyester resins, ET-2900, made by SK Chemical) 5 parts
Methacrylic acid 1 part
Cross-linker(divinylbenzen, made by Aldrich) 0.5 part
di-tert-buthyl salicylic acid aluminum compound(E-108, made by Orientchemical) 1 part

[0087] After dispersing the abovementioned components for 5 hours using Attritor(PE-075, made by Netzsch), a polymerizable monomer compounds was prepared by heating thereof at 60°**C**. A polymerizable monomer compounds is prepared by solving 4 parts of 2,2'-azobis(2,4-dimethylvaleronitril) as a polymerization starter in the styrene with maintaining 60°**C**, and then adding thereof to the polymerizable monomer compounds.

o Liquid droplet preparing process

[0088] A micronized polymerizable monomer mixture in dripped state was prepared by putting the abovementioned polymerizable monomer mixture into the water-borne dispersion medium solution under nitrogen gas flow, and stirring thereof at 10,000 RPM for 10 minutes at 60°C using TK type homomixer Mark II(made by Primix).

o Polymerization process

[0089] Fine particle suspension was prepared by stirring the polymerizable monomer mixture in dripped state not to sink or float after changing into Teflon stirring blade, and simultaneously carrying out polymerization for 5 hours at 75°C.
[0090] From the result of measuring the prepared fine particle suspension using Flow type particular analysis device FPIA-3000(made by Sysmax), average particle diameter (D50) is 0.83 μ**m**.

[Preparation Example 2] Preparation of Cyan Pigment Fine particle by Suspension Polymerization Process

[0091] The process of Preparation Example 1 was repeated except for changing Carbon black(first particle diameter 31nm) 5 parts to Cyan pigment(C.I. PB 15:3, made by Dainippon) 6 parts in the process of dispersing and dissolving the polymerizable monomer mixture of Preparation Example 1 to prepare cyan pigment fine particle suspension.
[0092] From the result of measuring the prepared fine particle suspension using Flow type particular analysis device FPIA-3000(made by Sysmax), average particle diameter (D50) is 0.75 μ**m.**

[Preparation Example 3] Preparation of Magenta Pigment Fine particle by Suspension Polymerization Process

[0093] The process of Preparation Example 1 was repeated except for changing Carbon black(first particle diameter 31nm) 5 parts to magenta pigment(PIGMENT RED122, made by Dainippon) 6 parts in the process of dispersing and dissolving the polymerizable monomer mixture of Preparation Example 1 to prepare magenta pigment fine particle suspension.
[0094] From the result of measuring the prepared fine particle suspension using Flow type particular analysis device FPIA-3000(made by Sysmax), average particle diameter(D50) is 0.82 μ**m.**

[Preparation Example 4] Preparation of Yellow Pigment Fine particle by Suspension Polymerization Process

[0095] The process of Preparation Example 1 was repeated except for changing Carbon black(first particle diameter 31nm) 5 parts to yellow pigment(PIGMENT YELLOW 180, made by Dainippon) 6 parts in the process of dispersing and dissolving the polymerizable monomer mixture of Preparation Example 1 to prepare magenta pigment fine particle suspension.
[0096] From the result of measuring the prepared fine particle suspension using Flow type particular analysis device FPIA-3000(made by Sysmax), average particle diameter(D50) is 0.75 μ**m.**

< Example of Preparing Fine particle by Seeded Polymerization Process >

o Dissolving/dispersing process of releasing agent

[0097] Ester wax(WE-4, made by NOF) as a releasing agent 20 parts, stearyl acrylate as a long-chain polymerizable monomer 2.5 parts, Anionic surfactant SDBS(Sodium Dodecyl Benzene Sulfonate) 20% aqueous solution 0.5 part and ion-exchanged water 300 parts were stirred using TK type homomixer Mark (made by Primix) at 10,000 RPM for 30 min in the condition of heating to 90**°C** under nitrogen gas flow to obtain releasing agent dispersion.

[0098] The releasing agent dispersion prepared as described above 35 parts and ion-exchanged water 250 parts were added to a stirrer, a heat-cooling device, a reflux device and a detachable reactor abled to insert each raw material (volume: 2 L), and stirred while heating to 90**°C** under nitrogen gas flow.

[0099] The abovementioned solution was stirred while slowly adding stylene 80 parts, n-butyl acrylate 20 parts, acrylic acid 1.5 parts, trichlorobromomethane 1.0 part thereto for 5 hours, and 2 weight% KPS (Potassium persulfate) 20 parts was added there to for 5 hours followed by additionally stirring thereof at 90**°C** for 1 hour.

[0100] After completing the polymerization reaction, the resulting solution was cooled to room temperature to obtain milk white releasing agent fine particle dispersion.

[0101] From the result of measuring the prepared fine particle dispersion containing releasing agent using Flow type particular analysis device FPIA-3000(made by Sysmax), average particle diameter(D50) is 0.7 μ**m**.

[Example 1]

[0102] An agglomerating process, heat fusing process, washing and drying process and addition process were performed as follows in a stirrer, a heat-cooling device, a reflux device and a detachable reactor abled to insert each raw material (volume: 2 L) to prepare a black toner.

o Agglomerating process

[0103] After maintaining the black pigment fine particle suspension by suspension polymerization process prepared in Preparation Example 1 85 parts and the fine particle dispersion by seeded polymerization process 15 parts at 60**°C,** the aggregation process carried out by slowly adding 5 parts of aluminum sulfate solution of 0.5 weight% thereto for 5 minutes until average particle diameter(D50) of final toner particles reaches to 6.5 μ**m**.

o Heat-fusing process

[0104] After the agglomerating process, the resulting solution was heated to 80**°C** for 1 hour followed by stirring at 150 RPM for 3 hours while maintaining the temperature at 80**°C.**

o Washing and drying process

[0105] Decompression filtering was carried out by cooling slurry obtained after the abovementioned heat fusing process, and then, after enough washing thereof many times using ion exchanged water 500 part, black toner particles, wherein average particle diameter(D50) was 6.8 μ**m** and the degree of rounding is 0.958, were obtained by drying thereof at 45**°C** decompression dryer during 24 hours.

o Addition process

[0106] Black toner particle having good fluidity is obtained by mixing hydrophobic silica(R972, made by Degu) 1 part with 100 parts of the black toner particles using multipurpose small mixing grinder(made by Mitsui mine).

[0107] The result of measuring black toner was shown in [table 1].

[Example 2]

[0108] An agglomerating process, heat fusing process, washing and drying process and addition process were performed as follows in a stirrer, a heat-cooling device, a reflux device and a detachable reactor abled to insert each raw material (volume: 2 L) to prepare a cyan toner.

o Agglomerating process

[0109] After maintaining the cyan pigment fine particle suspension by suspension polymerization process prepared in Preparation Example 2 85 parts and the fine particle dispersion by seeded polymerization process 15 parts at 60**°C,** the aggregation process carried out by slowly adding 5 parts of aluminum sulfate solution of 0.5 weight% thereto for 5 minutes until average particle diameter(D50) of final toner particles reaches to 6.5 μ**m.**

o Heat-fusing process

[0110] After the agglomerating process, the resulting solution was heated to 80°**C** for 1 hour followed by stirring at 150 RPM for 3 hours while maintaining the temperature at 80**°C**.

o Washing and drying process

[0111] Decompression filtering was carried out by cooling slurry obtained after the abovementioned heat fusing process, and then, after enough washing thereof many times using ion exchanged water 500 part, cyan toner particles, wherein average particle diameter(D50) was 6.7 μ**m** and the degree of rounding is 0.951, were obtained by drying thereof at 45**°C** decompression dryer during 24 hours.

o Addition process

[0112] Cyan toner particle having good fluidity is obtained by mixing hydrophobic silica(R972, made by Degu) 1 part with 100 parts of the cyan toner particles using multipurpose small mixing grinder(made by Mitsui mine).

[0113] The result of measuring cyan toner was shown in [table 1].

[Example 3]

[0114] An agglomerating process, heat fusing process, washing and drying process and addition process were performed as follows in a stirrer, a heat-cooling device, a reflux device and a detachable reactor abled to insert each raw material (volume: 2 L) to prepare a magenta toner.

o Agglomerating process

[0115] After maintaining the magenta pigment fine particle suspension by suspension polymerization process prepared in Preparation Example 3 85 parts and the fine particle dispersion by seeded polymerization process 15 parts at 60**°C**, the aggregation process carried out by slowly adding 5 parts of aluminum sulfate solution of 0.5 weight% thereto for 5 minutes until average particle diameter(D50) of final toner particles reaches to 6.5 μ**m**.

o Heat-fusing process

[0116] After the agglomerating process, the resulting solution was heated to 80**°C** for 1 hour followed by stirring at 150 RPM for 3 hours while maintaining the temperature at 80**°C.**

o Washing and drying process

[0117] Decompression filtering was carried out by cooling slurry obtained after the abovementioned heat fusing process, and then, after enough washing thereof many times using ion exchanged water 500 part, magenta toner particles, wherein average particle diameter(D50) was 6.7 μ**m** and the degree of rounding is 0.948, were obtained by drying thereof at 45**°C** decompression dryer during 24 hours.

o Addition process

[0118] Magenta toner particle having good fluidity is obtained by mixing hydrophobic silica(R972, made by Degu) 1 part with 100 parts of the cyan toner particles using multipurpose small mixing grinder(made by Mitsui mine).

[0119] The result of measuring magenta toner was shown in [table 1].

[Example 4]

[0120] An agglomerating process, heat fusing process, washing and drying process and addition process were performed as follows in a stirrer, a heat-cooling device, a reflux device and a detachable reactor abled to insert each raw material (volume: 2 L) to prepare a yellow toner.

o Agglomerating process

[0121] After maintaining the yellow pigment fine particle suspension by suspension polymerization process prepared in Preparation Example 4 85 parts and the fine particle dispersion by seeded polymerization process 15 parts at 60**°C,** the aggregation process carried out by slowly adding 5 parts of aluminum sulfate solution of 0.5 weight% thereto for 5 minutes until average particle diameter(D50) of final toner particles reaches to 6.5 μ**m**.

o Heat-fusing process

[0122] After the agglomerating process, the resulting solution was heated to 80**°C** for 1 hour followed by stirring at 150 RPM for 3 hours while maintaining the temperature at 80**°C.**

o Washing and drying process

[0123] Decompression filtering was carried out by cooling slurry obtained after the abovementioned heat fusing process, and then, after enough washing thereof many times using ion exchanged water 500 part, yellow toner particles, wherein average particle diameter(D50) was 6.5 μ**m** and the degree of rounding is 0.950, were obtained by drying thereof at 45**°C** decompression dryer during 24 hours.

o Addition process

[0124] Yellow toner particle having good fluidity is obtained by mixing hydrophobic silica(R972, made by Degu) 1 part with 100 parts of the cyan toner particles using multipurpose small mixing grinder(made by Mitsui mine).

[0125] The result of measuring magenta toner was shown in [table 1].

[Comparative Example 1]

o Inorganic dispersion medium preparing process

[0126]

Ion-exchanged water 900 parts
Na_3PO_4 3.4 parts
$CaCl_2$ 3.8 parts

[0127] In the condition of heating the abovementioned components to 60**°C**, water-borne dispersion medium containing hydoxyapatite(generation theorectical quantity: 1.5 parts by weight) which is insoluble microparticular dispersion stabilizer was obtained by stirring the abovementioned components at 10,000 RPM using TK type homomixer Mark (made by Primix).

o Polymerizable monomer mixture dispersing and dissolving process

[0128]

Styrene 80 parts
n-butyl acrylate 20 parts
Paraffin wax(melting point 72**°C**) 10 parts
Carbon black(first particle diameter 31nm) 5 parts
Polar resins(Polyester resins, ET-2900, made by SK Chemical) 5 parts
Methacrylic acid 1 part
Cross-linker(divinylbenzen) 0.5 part
di-tert-buthyl salicylic acid aluminum compound(E-108, made by Orientchemical) 1 part

[0129] After dispersing the abovementioned components during 5 hours using Attritor(PE-075, made by Netzsch), a polymerizable monomer compounds was prepared by heating thereof at 60**°C.** A polymerizable monomer compounds was prepared by dissolving 4 parts of 2,2'-azobis(2,4-dimethylvaleronitril) as a polymerization starter in the styrene with maintaining 60**°C,** and then adding thereof to the polymerizable monomer compounds.

o Liquid droplet preparing process

[0130] A polymerizable monomer mixture in dripped state was prepared by putting the abovementioned polymerizable monomer compounds into the inorganic dispersion medium solution under nitrogen gas flow, and stirring thereof at 6,000 RPM for 10 minutes at 60**°C** using TK type homomixer.

o Polymerization process

[0131] Toner particles were prepared by stirring the polymerizable monomer mixture in dripped state not to sink or float after changing into Teflon stirring blade, and simultaneously carrying out polymerization for 8 hours at 70°C.

o Washing and Drying process

[0132] Decompression filtering was carried out by cooling slurry obtained after the abovementioned fusing process, adding 5N hydrochloric acid for pH to maintain below 2, thereby for the inorganic dispersion medium to be solved.

[0133] Then, after enough washing thereof many times using ion exchanged water 500 part, compared toner particles 1 were obtained by drying thereof at 45**°C** decompression dryer during 24 hours.

[0134] From the result of measuring the prepared toner particles using Flow type particular analysis device FPIA-3000 (made by Sysmax), average particle diameter(D50) was 7.5 μ**m**, and a degree of rounding is 0.978.

o Addition process

[0135] Black compared toner 1 having good fluidity was obtained by mixing hydrophobic silica 1 part with 100 parts of the compared toner particles 1 using multipurpose small mixing grinder(made by Mitsui mine).

[0136] The result of measuring black compared toner was shown in [table 1].

[0137] Hereinafter, the toners prepared in Examples and Comparative Example were evaluated as follows.

<Charge-to-mass ratio>

[0138] Toner 0.5 g and carrier 9.5 g were put into a PE bottle, and mixed using a Turbula Mixer at 150 RPM for 5 minutes. Then charge-to-mass ratio of the resulting mixture was measured using a suction toner charge-to-mass ratio measuring apparatus(made by TREK, Model : 210HS-2).

<Toner Consumption>

[0139] 1,000 pages were printed using the toners prepared in Examples and Comparative Example in CP-1215 printer made by Hewlett Packard(HP) under 23°C / 50 % condition with ISO toner consumption standard pattern, and the toner usage was measured to evaluate the toner consumption.

[table 1]

No.	Final Toner Particle			Charge-To-Mass Ratio (μC/g)	Toner Consumption (g/ 1000 page)
	Average Particle Diameter (μm) (D50)	Degree of Rounding	Particle Size Distribution*1 (D90/D10)		
Exam. 1	6.8	0.958	1.8	-21.7	21.3
Exam. 2	6.7	0.951	1.9	-20.5	20.7
Exam. 3	6.7	0.948	1.9	-20.9	18.2
Exam. 4	6.5	0.950	2.0	-20.4	20.2

(continued)

No.	Final Toner Particle			Charge-To-Mass Ratio (μC/g)	Toner Consumption (g/1000 page)
	Average Particle Diameter (μm) (D50)	Degree of Rounding	Particle Size Distribution*1 (D90/D10)		
Comp. Exam. 1	7.5	0.978	4.5	-9.9	32.5
*1: the lower particle size distribution(D90/D10) value represents the narrower particle distribution, and the higher value represents the wider particle distribution.					

INDUSTRIAL APPLICABILITY

[0140] The method for producing a toner composition according to the present invention is easy to control particle diameter and rounded image, and also provides an electrostatic image developing toner having uniform distribution of particle size in comparison to prior toner producing processes and, thus its toner consumption is low and is useful to an electro photographic process requiring high resolution.

[0141] While the invention will be described in conjunction with exemplary embodiments, it will be understood that present description is not intended to limit the invention to those exemplary embodiments. On the contrary, the invention is intended to cover not only the exemplary embodiments, but also various alternatives, modifications, equivalents and other embodiments, which may be included within the spirit and scope of the invention as defined by the appended claims.

Claims

1. A toner composition comprising binding resin forming monomers, coloring agents, dispersion stabilizers, charge control agents, releasing agents, polar resins or polar monomers, being prepared by the method comprising:

(1) a suspension polymerization process(S1) comprising:

1-1) a step of preparing an water-borne dispersion medium,
1-2) a step of dispersing and dissolving a polymerizable monomer mixture,
1-3) a liquid droplet-preparing step of micronizing the liquid prepared in the step 1-2) into the liquid prepared in the step 1-1) with high shearing force, and
1-4) a step of radically polymerizing the fine particle liquid droplet prepared in the step 1-3);

(2) a seeded polymerization process(S2) comprising:

2-1)a step of dissolving and dispersing the releasing agent, and

2-2) a step of the seeded polymerization of the liquid prepared in the step 2-1);

(3) a process of agglomerating particles produced in the suspension polymerization process(S1) and particles in the seeded polymerization process(S2) each other to make agglomerate;
(4) a process of fusing the particles agglomerated in the process(3) by heat;
(5) a process of washing and drying the toner produced in the process(4); and
(6) a process of adding an agent for providing the toner produced in the process (5) with electrostatic properties and fluidity.

2. The toner composition according to claim 1, wherein the average particle diameter of the particles prepared by the suspension polymerization process(S1) is 50 nm to 10 μm.

3. The toner composition according to claim 1, wherein the average particle diameter of the releasing agent particles prepared by the seeded polymerization process(S2) is 50 nm to 10 μm.

4. The toner composition according to claim 1, wherein the releasing agent of the seeded polymerization process(S2)

is at least one releasing agent selected from the group consisting of paraffin-based wax, ester-based wax, micro crystal wax, montan-based wax, Fischer-Tropsch wax, polyethylene wax, polypropylene wax and carnauba wax.

5. The toner composition according to claim 1, wherein an amount of the releasing agent is 0.5 part to 20 parts by weight for 100 parts by weight of the polymerizable monomer.

6. The toner composition according to claim 1, wherein DSC maximum heat absorption peak of the releasing agent is 40°C to 120°C.

7. The toner composition according to claim 1, wherein the polar resin is at least one polar resin selected from the group consisting of polyester resin and polystyrene copolymer resin.

8. The toner composition according to claim 1, wherein the polar monomer is at least one polar monomer selected from the group consisting of acrylic acid, methacrylic acid, itaconic acid, maleic acid and fumaric acid.

9. The toner composition according to claim 1, wherein the charge control agent is at least one charge control agent selected from the group consisting of dibutyl salicylic acid, naphthoeic acid, dicarboxylic acid, dibutyl salicylic acid aluminum compound, dibutyl salicylic acid zinc compound, dibutyl salicylic acid zirconium compound, dibutyl salicylic acid chrome compound, nigrosine-based compound, quaternary ammonium salt and imidazole compound.

10. The toner composition according to claim 9, wherein an amount of the charge control agent is 0.5 parts to 10 parts by weight for 100 parts by weight of the polymerizable monomer.

11. The toner composition according to claim 1, wherein the degree of rounding of the final toner particles is 0.9 to 0.99.

12. A method for preparing toner composition comprising binding resin forming monomers, a coloring agent, dispersion stabilizers, charge control agents, releasing agent, polar resins or polar monomers, being prepared by the method comprising:

(1) a suspension polymerization process(S1) comprising:

1-1) a step of preparing an water-borne dispersion medium,
1-2) a step of dispersing and dissolving a polymerizable monomer mixture,
1-3) a liquid droplet-preparing step of micronizing the liquid prepared in the step 1-2) into the liquid prepared in the step 1-1) with high shearing force, and
1-4) a step of radically polymerizing the fine particle liquid droplet prepared in the step 1-3);

(2) a seeded polymerization process(S2) comprising:

2-1) a step of dissolving and dispersing the releasing agent, and
2-2) a step of the seeded polymerization of the liquid prepared in the step 2-1);

(3) a process of agglomerating particles produced in the suspension polymerization process(S1) and particles in the seeded polymerization process(S2) each other to make agglomerate;
(4) a process of fusing the particles agglomerated in the process(3) by heat;
(5) a process of washing and drying the toner produced in the process(4); and
(6) a process of adding an agent for providing the toner produced in the process (5) with electrostatic properties and fluidity.

13. The method for preparing toner composition according to claim 12, wherein the average particle diameter of the particles prepared by the suspension polymerization process(S1) is 50 nm to 10 μm.

14. The method for preparing toner composition according to claim 12, wherein the average particle diameter of the releasing agent particles prepared by the seeded polymerization process(S2) is 50 nm to 10 μm.

15. The method for preparing toner composition according to claim 12, wherein the releasing agent of the seeded polymerization process(S2) is at least one releasing agent selected from the group consisting of paraffin-based wax, ester-based wax, micro crystal wax, montan-based wax, Fischer-Tropsch wax, polyethylene wax, polypropylene

wax and carnauba wax.

16. The method for preparing toner composition according to claim 12, wherein the aggregation agent is at least one aggregation agent selected from the group consisting of an inorganic salts having monovalent metallic cations, an inorganic salts having divalent metallic cations and an inorganic salts having trivalent metallic cations.

17. The method for preparing toner composition according to claim 16, wherein the inorganic salt having monovalent metallic cations is at least one inorganic salt selected from the group consisting of NaCl, KCl, LiCl, Na_2SO_4, K_2SO_4, Li_2SO_4, CH_3COONa and $C_6H_5SO_3Na$; the inorganic salt having divalent metallic cations is at least one inorganic salt selected from the group consisting of $MgCl_2$, $CaCl_2$, $MgSO_4$, $CaSO_4$ and $ZnSO_4$; and the inorganic salt having trivalent metallic cations is at least one inorganic salt selected from the group consisting of $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$.

18. The method for preparing toner composition according to claim 12, wherein the aggregation temperature in aggregating is 5°C to 80°C.

19. The method for preparing toner composition according to claim 12, wherein the degree of rounding of the final toner particles is 0.9 to 0.99.

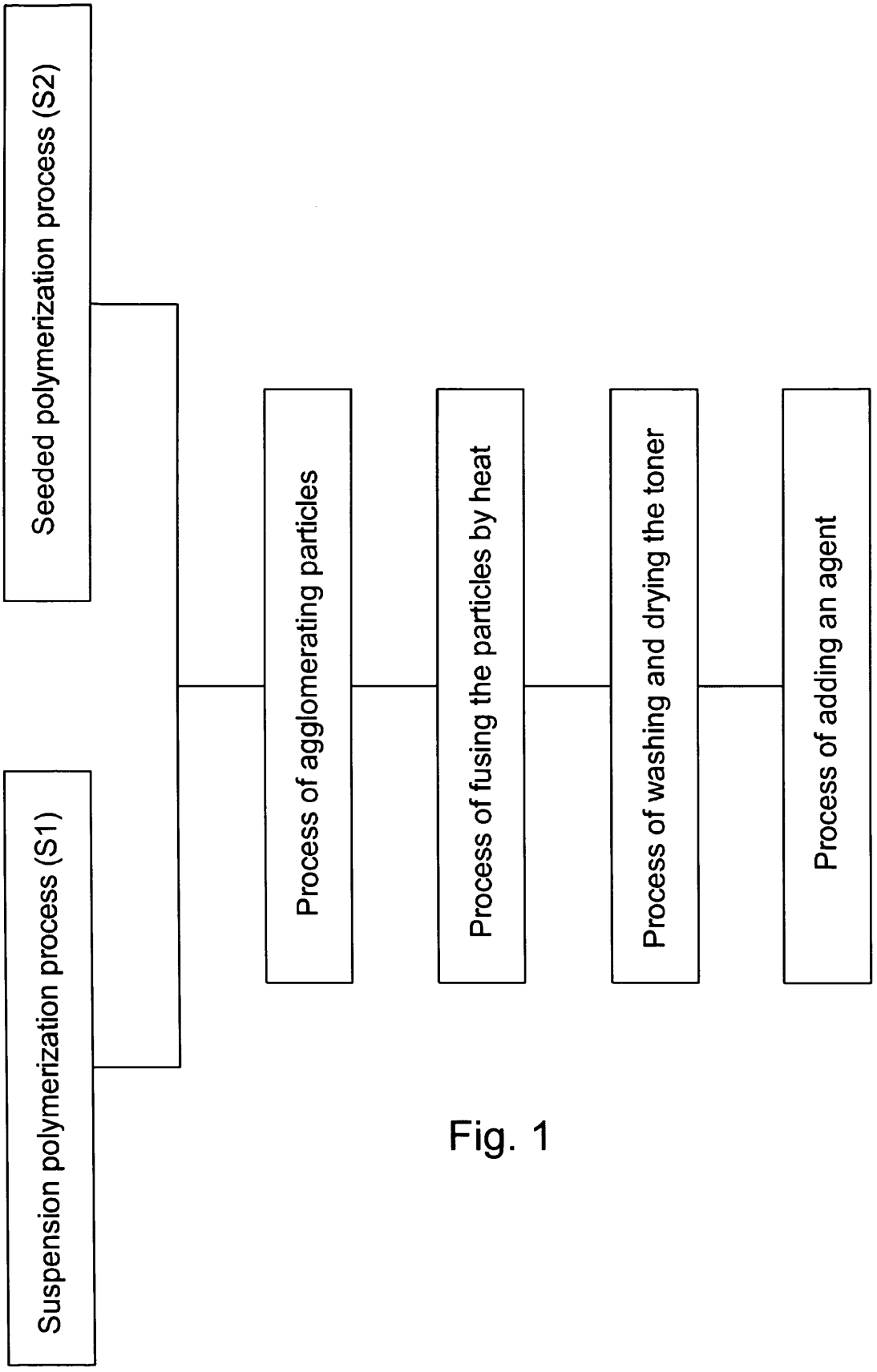
Seeded polymerization process (S2)
Suspension polymerization process (S1)
Process of agglomerating particles
Process of fusing the particles by heat
Process of washing and drying the toner
Process of adding an agent

Fig. 1

REFERENCES CITED IN THE DESCRIPTION

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