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(54) Title: TONER FOR DEVELOPING ELECTROSTATIC IMAGE, AND TONER-SUPPLYING MEANS AND APPARATUS FOR FORMING IMAGE HAVING THE SAME

(57) Abstract: Provided is a toner for developing electrostatic images. The toner comprises a plurality of toner particles, in which each toner particle of the plurality of toner particles includes a core particle including a first binder resin, a colorant, and a releasing agent and a shell layer coating the core particle and including a second binder resins. The first binder resin of the core particle comprises about 80 wt% or more of a first amorphous polyester resin and about 20 wt% or less of a crystalline polyester resin, based on a total weight of the first binder resin, and the second binder resin comprises a second amorphous polyester resin, wherein the first amorphous polyester resin, the crystalline polyester resin, and the releasing agent respectively have solubility parameters that satisfy conditions (1), (2), (3), and (4).



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TITLE

TONER FOR DEVELOPING ELECTROSTATIC IMAGE, AND TONER-SUPPLYING MEANS AND APPARATUS FOR FORMING IMAGE HAVING THE SAME

BACKGROUND

[0001] Methods of preparing toner particles suitable for an electrophotographic process or an electrostatic image recording process to develop electrostatic images in electrophotographic copiers, laser printers, electrostatic recording apparatuses, and the like may be largely classified into a pulverization method and a polymerization method.

[0002] Recently, among methods of preparing toners used in an imaging apparatus, a polymerization method, which is relatively simple and can easily adjust particle diameters of toner, has received much attention. With heightened interest in durability and environmental friendliness of members constituting the imaging apparatuses and energy saving, interest in low-temperature fixability has increased.

[0003] A core-shell type toner particle as disclosed in US Pat. No. 6,617,091 has been suggested as one of the ways of improving low-temperature fixability. According to the method, charging deviation between colors may be reduced by inhibiting exposure of pigment surfaces.

DETAILED DESCRIPTION

[0004] When a toner includes a high wax content, for example, plasticization may easily occur due to partial miscibility between the binder resin and a low molecular weight portion of the wax, resulting in deterioration in terms of high-temperature storage ability or cohesiveness of the toner. Also, a method of encapsulating a surface of a binder resin with another binder resin having a relatively high glass transition temperature (T_g) has been suggested to prevent a decrease in T_g of the binder resin caused for improving low-temperature

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fixability. However, although excellent low-temperature fixability may be obtained in this case, high-temperature storage ability may not be sufficient.

[0005] As used herein, the term "and/or" includes any and all combinations of one or more of the associated listed items. Expressions such as "at least one of," when preceding a list of elements, modify the entire list of elements and do not modify the individual elements of the list.

[0006] A toner for developing electrostatic images according to the present disclosure may include a plurality of toner particles, each toner particle including: a core particle including a first binder resin, a colorant, and a releasing agent; and a shell layer coating the core particle and including a second binder resin. The first binder resin of the core particle includes about 80 wt% or more of an amorphous polyester resin and about 20 wt% or less of a crystalline polyester resin based on a total weight of the first binder resin, and the second binder resin includes an amorphous polyester resin. The amorphous polyester resin, the crystalline polyester resin, and the releasing agent may satisfy the following conditions (1), (2), (3), and (4):

$$1.0 \text{ (J/cm)}^{1/2} \leq \text{SP(A)} - \text{SP(C)} \leq 2.0 \text{ (J/cm)}^{1/2} \quad (1),$$

$$2.5 \text{ (J/cm)}^{1/2} \leq \text{SP(A)} - \text{SP(W)} \quad (2),$$

$$\text{SP(C)} - \text{SP(W)} \leq 1.6 \text{ (J/cm)}^{1/2} \quad (3), \text{ and}$$

$$\text{SP(C)} - \text{SP(W)} \leq \text{SP(A)} - \text{SP(C)} \quad (4).$$

[0007] In this regard, SP(A), SP(C), and SP(W) are solubility parameters ((J/cm)^{1/2}) of the amorphous polyester resin, the crystalline polyester resin, and the releasing agent, respectively.

[0008] According to examples, a weight average molecular weight Mw(C), a weight percentage Wt(C) based on a total weight of the toner, and a melting point Tm(C) of the crystalline polyester resin may satisfy the following conditions (5) and (6):

$$2.5 \text{ kDa/wt\%} \leq \text{Mw(C)}/\text{Wt(C)} \leq 5.0 \text{ kDa/wt\%} \quad (5), \text{ and}$$

$$60 \text{ }^{\circ}\text{C} \leq \text{Tm(C)} \leq 90 \text{ }^{\circ}\text{C} \quad (6),$$

[0009] In this regard, Mw(C) is a weight average molecular weight (unit: kiloDalton (kDa) = 1,000 g/mol) of the crystalline polyester resin measured by

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gel permeation chromatography (GPC) performed on a tetrahydrofuran(THF)-soluble fraction of the crystalline polyester resin, Wt(C) is a weight percentage (unit wt%) of the crystalline polyester resin based on a total weight of the toner, and Tm(C) is a melting point (unit: °C) of the crystalline polyester.

[0010] According to another example, a weight average molecular weight Mw(A) and a glass transition temperature Tg(A) of the amorphous polyester resin may further satisfy the following conditions (7) and (8):

$$12.0 \text{ kDa} \leq \text{Mw(A)} \leq 25.0 \text{ kDa} \quad (7), \text{ and}$$

$$55 \text{ }^{\circ}\text{C} \leq \text{Tg(A)} \leq 70 \text{ }^{\circ}\text{C} \quad (8),$$

[0011] In this regard, Mw(A) is a weight average molecular weight (unit: kDa) of the amorphous polyester resin measured by GPC performed on a THF-soluble fraction of the amorphous polyester resin, and Tg(C) is a glass transition temperature (unit: °C) of the amorphous polyester resin.

[0012] According to examples, the releasing agent may include at least one selected from a polyethylene-based wax, a polypropylene-based wax, a silicone-based wax, a paraffin-based wax, an ester-based wax, a carnauba-based wax, and a metallocene-based wax.

[0013] According to examples, a volume average particle diameter of the toner is from about 3 μm to about 9 μm.

[0014] According to examples, an average circularity of the toner is from about 0.940 to about 0.980.

[0015] According to examples, a volume average geometric size distribution coefficient (GSDv) and a number average geometric size distribution coefficient (GSDp) of the toner are about 1.30 or less and about 1.25 or less, respectively.

[0016] A toner supply device according to the present disclosure includes the toner for developing electrostatic images according to the present disclosure. Particularly, the toner supply device may include: a toner tank in which toner may be stored; a supply part protruding from an inner surface of the toner tank to externally supply toner from the toner tank; and a toner-agitating member rotatably disposed inside the toner tank to agitate toner in the inner space of the toner tank comprising a space above a top surface of the supplying part.

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[0017] An imaging apparatus according to the present disclosure includes the toner for developing electrostatic images according to the present disclosure. Particularly, the imaging apparatus may include: an image carrier; an image forming device configured to form an electrostatic image, for example, particularly an electrostatic latent image, on a surface of the image carrier; a toner storing device, such as the toner tank above, in which toner may be stored; a toner supplying device configured to supply the toner to the surface of the image carrier to develop the electrostatic image into a visible image on the surface of the image carrier; and a transferring device configured to transfer the visible image from the surface of the image carrier to an image receiving member, wherein the toner is the toner for developing electrostatic images according to the present disclosure.

[0018] A method of forming an image according to the present disclosure includes forming a visible image by attaching toner to a surface of an image carrier on which an electrostatic image is formed and transferring the visible image to an image receiving member, wherein the toner is the toner for developing electrostatic images according to the present disclosure.

[0019] Hereinafter, a toner for developing electrostatic images and a method of preparing the same according to examples of the present disclosure will be described in detail.

[0020] The toner for developing electrostatic images according to examples of the present disclosure is prepared by adjusting amounts and physical properties, such as solubility parameters, thermal properties, and molecular weights, of a crystalline polyester having sharp melting characteristics, an amorphous polyester capable of improving low-temperature fixability, and a releasing agent. Particularly, in the toner, compatibilization caused by trans-esterification, and/or other mechanism between the crystalline polyester and the amorphous polyester may be minimized by satisfying at least the above-described conditions (1), (2), (3), and (4). Accordingly, a domain size and distribution of the releasing agent, a domain size and distribution of the crystalline polyester resin, and a change in thermal properties of the toner may be appropriately adjusted in toner particles. As a result, the toner may maintain sharp melting

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characteristics of the crystalline polyester and a high T_g of the amorphous polyester. Thus, the toner may efficiently obtain stable durability due to wide fixing offset range, high fixing gloss, and good surface shapes of toner particles. Thus, the toner according to examples of the present disclosure may have excellent low-temperature fixability, wide fixing or fusing latitude, high gloss, high fluidity, and excellent surface characteristics of particles (i.e., excellent high-temperature storage ability and durability) via morphology control based on the above-described concepts.

[0021] The toner for developing electrostatic images according to examples of the present disclosure includes a plurality of toner particles. Each toner particle has a core-shell structure including a core particle including a first binder resin, a colorant, and a releasing agent and a shell layer coating the core particle and including a second binder resin.

[0022] The first binder resin of the core particle includes about 80 wt% or more of an amorphous polyester resin and about 20 wt% or less of a crystalline polyester resin based on a total weight of the first binder resin, and the second binder resin includes an amorphous polyester resin. The first binder resin may include about 80 wt% or more of the amorphous polyester resin, particularly, about 80 wt% to about 99 wt% or about 80 wt% to about 97 wt% of the amorphous polyester resin and about 20 wt% or less of the crystalline polyester resin, particularly, about 1 wt% to about 20 wt% or about 3 wt% to about 20 wt% of the crystalline polyester resin based on a total weight of the first binder resin. Polyester resins may efficiently enhance color reproducibility. When the first binder resin of the core particle includes about 80 wt% or more of the amorphous polyester resin and about 20 wt% or less of the crystalline polyester resin based on a total weight of the first binder resin, the toner particles may have high strength and excellent low-temperature fixability, excellent high-temperature storage ability, and excellent charging characteristics, and deterioration of image quality due to contamination of members, such as an image forming device or, a photoconductor drum, of the imaging apparatus employing the toner may be efficiently inhibited in the imaging apparatus.

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[0023] The crystalline polyester resin refers to a polyester resin that shows a definite or sharp endothermic peak representing fusion or melting of crystallites in a differential scanning calorimetry (DSC) thermogram. For example, the crystalline polyester resin may be defined as a polyester resin that has a full width at half maximum (FWHM) of the endothermic peak of 15 °C or less in a DSC thermogram which is obtained using a temperature increasing rate of 10 °C/min. The crystalline polyester resin is used to improve image gloss and low-temperature fixability of the toner. The amorphous polyester resin refers to a polyester resin that does not show a definite or sharp endothermic peak representing fusion or melting of crystallites in a DSC thermogram. For example, the amorphous polyester resin may be defined as a polyester resin that exhibits a stepwise change (a so-called "base line shift" phenomenon) in an amount of heat absorption or has a FWHM of the endothermic peak of the amorphous polyester resin which is greater than 15 °C in a DSC thermogram which is obtained using a temperature increasing rate of 10 °C/min. The melting point T_m of the crystalline polyester resin may be from about 60 °C to about 100 °C, for example, from about 60 °C to about 95 °C, from about 60 °C to about 90 °C, from about 62 °C to about 90 °C, from about 63 °C to about 80 °C, from about 65 °C to about 75 °C, or from about 65 °C to about 70 °C. When the melting point of the crystalline polyester resin is from about 60 °C to about 100 °C, for example, from about 60 °C to about 90 °C, aggregation of toner particles may be efficiently inhibited, preservability of fixed images may be improved, and low-temperature fixability may be enhanced. The glass transition temperature T_g of the amorphous polyester resin may be from about 50 °C to about 75 °C, for example, from about 55 °C to about 70 °C, or from about 60 °C to about 70 °C, or from about 62 °C to about 69 °C.

[0024] When the crystalline polyester resin is added to the amorphous polyester resin, the toner has high fixability near a melting temperature of the crystalline polyester resin according to sharp melting characteristics of the crystalline polyester resin, i.e., according to an effect of remarkable reduction of viscosity

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as the crystalline polyester resin quickly melts at a narrow temperature range near the melting temperature. When a crystalline polyester resin having a relatively low melting point (equal to or greater than T_g of the amorphous polyester resin) is used within a range of maintaining durability and high-temperature storage characteristics of the toner, the toner may have quick and high fixability at a low-temperature. In other words, the high T_g of the amorphous polyester resin is maintained by suitably mixing the crystalline polyester resin and the amorphous polyester resin, and the toner has a remarkably reduced viscosity at a fixing temperature according to the sharp melting characteristics of the crystalline polyester resin. Thus, high-temperature storage characteristics are maintained while obtaining low-temperature fixability. However, in order to effectively realize such characteristics, the compatibility of the crystalline and amorphous polyester resins is necessarily controlled.

[0025] Generally, when two types of polyester are mixed together by melting, an ester exchange reaction, i.e., trans-esterification, occurs between ester groups of the two types of polyester, and thus the mixture of two types of polyester changes to a copolymer form. The copolymer is at first in a block copolymer form, but as compatibilization proceeds, the copolymer gradually changes to a random copolymer form. Accordingly, it is difficult to crystallize due to the irregularity of a polymer chain, and a plasticization effect, wherein a melting temperature and a glass transition temperature of the mixture or the copolymer are shifted to a lower temperature side, may occur. Consequently, the durability and storage characteristics of the toner may deteriorate.

[0026] The toner according to the examples of the present disclosure may be prepared by preparing latex (emulsion) of each polyester resin in such a way that the particle size is from about 100 to about 300 nm, and then growing the particle size to be used as the toner through an aggregation and coalescence process after mixing. The aggregation process may be performed at T_g of the amorphous polyester resin or below, but the coalescence process may be performed at T_g of the amorphous polyester resin and the melting temperature of the crystalline polyester resin or above. Accordingly, each polyester resin maintains a molten state for about 2 to about 3 hours during the coalescence

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process, and thus the compatibilization inevitably proceeds. Thus, when it is difficult to crystallize due to compatibilization, sharp melting characteristics disappear and thus low-temperature fixability may not be obtained. However, since a proceeding speed of compatibilization depends on compatibility between two polymers, molecular structure design of polyester resins used to prepare toner is necessary. In the toner according to the examples, compatibility between a polyester binder resin and a releasing agent is strictly controlled by designing the crystalline polyester resin and the amorphous polyester resin of the core particle according to the above-described conditions such that the melting temperature of the crystalline polyester resin and the T_g of the amorphous polyester resin do not remarkably change after the toner is prepared, thereby satisfactorily maintaining high-temperature storage characteristics, low-temperature fixability, wide fusing latitude, and high gloss of the toner.

[0027] Polyester resins may be prepared by reacting an aliphatic, an alicyclic, or an aromatic polycarboxylic acid (polycarboxylic acid) or an alkyl ester thereof with a polyhydric alcohol, e.g., an aliphatic polyhydric alcohol through a direct esterification reaction or trans-esterification reaction.

[0028] In detail, the crystalline polyester resin may be prepared by reacting an aliphatic polycarboxylic acid having at least C₈ (excluding carbon atoms of the carboxyl groups), for example, from C₈ to C₁₂, in detail, from C₉ to C₁₀, with an aliphatic alcohol having at least C₈, for example, from C₈ to C₁₂, in detail, from C₁₀ to C₁₂. For example, the crystalline polyester resin may be obtained by reacting 1,9-nonanediol and 1,10-decane dicarboxylic acid, or 1,9-nonanediol and 1,12-dodecane dicarboxylic acid. If the numbers of carbon atoms for the aliphatic polycarboxylic acid and the aliphatic polyhydric alcohol are within the above ranges, the crystalline polyester resin may have a melting temperature suitable to be used for toner. In addition, such crystalline polyester resin has a higher linearity, and thus has a higher affinity to the amorphous polyester resin.

[0029] The crystalline polyester resin may have a weight average molecular weight M_w of, for example, from about 8,000 g/mol to about 60,000 g/mol, particularly, from about 10,000 g/mol to about 50,000 g/mol, from about 13,000

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g/mol to about 40,000 g/mol, from about 15,000 g/mol to about 35,000 g/mol, from about 15,000 g/mol to about 32,000 g/mol, from about 17,000 g/mol to about 32,000 g/mol, from about 18,000 g/mol to about 30,000 g/mol, or from about 18,000 g/mol to about 28,000 g/mol, when measured for a tetrahydrofuran (THF)-soluble fraction by gel permeation chromatography (GPC). When the weight average molecular weight M_w satisfies the above-described ranges, low-temperature fixability and anti-hot offset characteristics may be effectively improved and a decrease in the strength of the resin may be prevented, thereby improving the strength of an image fixed on a paper. In addition, since a decrease in the glass transition temperature of the toner may be inhibited, storage characteristics, such as anti-blocking characteristics, of the toner may also be improved.

[0030] The polyester resin may be prepared at a polymerization temperature of about 180°C to about 230°C, in a reaction system under a reduced pressure if needed, while water or alcohol produced during condensation reaction is removed.

[0031] When a polymerizable monomer is not dissolved or compatible at a reaction temperature, a solvent having a high boiling point may be added thereto as a solubilizer to dissolve the polymerizable monomer. Polycondensation may be performed while removing a solubilizer by distillation.

[0032] Examples of a catalyst that may be used in the preparation of the crystalline polyester resin include, but are not limited to, a compound of an alkaline metal such as sodium and lithium, a compound of an alkaline earth metal such as magnesium and calcium, a compound of a metal such as zinc, manganese, antimony, titanium, tin, zirconium, and germanium; a phosphorous acid compound; a phosphoric acid compound; or an amine compound.

[0033] Examples of polycarboxylic acids that may be used to obtain the amorphous polyester resin include phthalic acid, isophthalic acid, terephthalic acid, tetrachlorophthalic acid, chlorophthalic acid, nitrophthalic acid, p-carboxyphenyl acetic acid, p-phenylene diacetic acid, m-phenylene diglycolic acid, p-phenylene diglycolic acid, o-phenylene diglycolic acid, diphenylacetic acid, diphenyl-p,p'-dicarboxylic acid, naphthalene-1,4-dicarboxylic acid, naphthalene-1,5-

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dicarboxylic acid, naphthalene-2,6-dicarboxylic acid, anthracenedicarboxylic acid, and/or cyclohexanedicarboxylic acid. Examples of polycarboxylic acids, excluding dicarboxylic acids, include trimellitic acid, pyromellitic acid, naphthalenetetracarboxylic acid, naphthalenetetracarboxylic acid, pyrenetetracarboxylic acid, pyrenetetracarboxylic acid. An acid anhydride, an acid chloride, or an ester may also be used instead of the carboxylic acids in which the carboxylic groups of the carboxylic acids are converted to an anhydride group, an acyl chloride group, or an ester group, respectively. For example, terephthalic acid or a lower ester thereof, diphenylacetic acid, or cyclohexane dicarboxylic acid, among the polyvalent cyclic acids listed above, may be used. In this regard, a lower ester means an ester of a C1-C8 aliphatic alcohol.

[0034] Examples of the polyhydric alcohol that may be used to obtain the amorphous polyester resin include aliphatic diols, such as ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, butanediol, hexanediol, neopentyl glycol, and glycerine; alicyclic diols, such as cyclohexane diol, cyclohexane dimethanol, and hydrogenated bisphenol A; and aromatic diols, such as an ethylene oxide adduct of bisphenol A and a propylene oxide adduct of bisphenol A. One or at least two of these polyhydric alcohols may be used. These polyhydric alcohols may be used alone or in a combination of at least two thereof. For example, aromatic diols or alicyclic diols, among the polyhydric alcohols listed above, may be used. In this regard, aromatic diols may be used. In order to ensure excellent fixability, trihydric or higher alcohols, such as glycerin, trimethylolpropane, or pentaerythritol, may be used together with diols to provide a cross-linked or branched structure.

[0035] The amorphous polyester resin may be prepared by condensating the polyhydric alcohol and the polycarboxylic acid according to a general method. For example, the polyhydric alcohol and the polycarboxylic acid are mixed, together with a catalyst, if necessary, in a reaction vessel equipped with a thermometer, a stirrer, and a condenser, e.g., a down flow type condenser, and heated at 150°C to 250°C in an inert gas (for example, nitrogen gas) until the mixture reaches a predetermined acid value, while residual low-molecular weight compounds are continuously removed from the reaction system. Then,

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the reaction product is cooled to obtain an amorphous polyester resin as a final reaction product.

[0036] Examples of a catalyst that may be used in the synthesis of the amorphous polyester resin include, but are not limited to, an antimony-based, a tin-based, a titanium-based, or an aluminum-based catalyst. For example, an esterification catalyst such as an organometallic compound, e.g., dibutyltin dilaurate or dibutyltin oxide or a metal compound, e.g., tetrabutyl titanate may be used. In terms of environmental influence and safety, a titanium-based compound or an aluminum-based compound may be used. The amount of the catalyst may be adjusted in the range of about 0.01 wt% to about 1.00 wt% based on a total amount of the reactants.

[0037] The amorphous polyester resin may have a weight average molecular weight M_w of, for example, from about 5,000 g/mol to about 60,000 g/mol, particularly, from about 10,000 g/mol to about 50,000 g/mol, from about 12,000 g/mol to about 45,000 g/mol, from about 12,000 g/mol to about 25,000 g/mol, from about 15,000 g/mol to about 40,000 g/mol, from about 15,000 g/mol to about 35,000 g/mol, from about 15,000 g/mol to about 30,000 g/mol, from about 15,000 g/mol to about 28,000 g/mol, from about 15,000 g/mol to about 27,000 g/mol, from about 15,000 g/mol to about 25,000 g/mol, from about 15,000 g/mol to about 22,000 g/mol, or from about 15,000 g/mol to about 20,000 g/mol, when measured for a tetrahydrofuran(THF)-soluble fraction by gel permeation chromatography (GPC). When the M_w satisfies the above-described ranges, low-temperature fixability and anti-hot offset characteristics may be improved and a decrease in strength of the resin may be suppressed, thereby improving the strength of an image fixed on a paper. In addition, since a decrease in the glass transition temperature of the toner may be inhibited, storage characteristics, such as anti-blocking characteristics, of the toner may also be improved.

[0038] The amorphous polyester resin of the first binder resin may be same as or different from the amorphous polyester resin of the second binder resin.

[0039] Since the releasing agent increases low-temperature fixability of the toner and durability and abrasion resistance of a final image, types and amounts of

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the releasing agent may greatly influence the characteristics of the toner. The releasing agent may prevent toner particles from adhering to the heating roller of a fixing device. The releasing agent may be a natural wax or a synthetic wax. Examples of the releasing agent include, but are not limited to, a polyethylene-based wax, a polypropylene-based wax, a silicone-based wax, a paraffin-based wax, an ester-based wax, a carnauba-based wax, a metallocene-based wax, and any mixture thereof.

[0040] . A melting point of the releasing agent may be from about 60 °C to about 100 °C, for example, from about 65 °C to about 90 °C, from about 65 °C to about 80 °C, from about 67 °C to about 77 °C, or from about 67 °C to about 75 °C. The releasing agent is physically attached to toner particles, but is not covalently bonded with toner particles.

[0041] The amount of the releasing agent contained in the core particle may be, for example, from about 1 part by weight to about 20 parts by weight, from about 2 parts by weight to about 16 parts by weight, or from about 3 parts by weight to about 12 parts by weight based on 100 parts by weight of the toner. When the amount of the releasing agent is 1 part by weight or more, excellent low-temperature fixability and a sufficient fixing temperature range may be obtained. When the amount of the releasing agent is 20 parts by weight or less, storage characteristics and economic feasibility may be improved.

[0042] The releasing agent may be an ester group-containing wax. Examples of the ester group-containing wax include (1) mixtures including an ester-based wax and a non-ester-based wax; and (2) an ester group-containing wax prepared by adding an ester group to a non-ester-based wax. Since an ester group has high affinity with respect to the binder component of the toner, the ester group-containing wax may be uniformly distributed among toner particles, and thus may effectively function. The non-ester-based wax may suppress an excessive plasticizing effect, which occur when an ester-based wax is exclusively used. Therefore, toner containing the mixture wax may retain satisfactory development characteristics for a long period of time.

[0043] Examples of the ester group-containing wax include a mixture including paraffin-based wax and an ester-based wax; and an ester group-containing

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paraffin-based wax. Specific examples thereof include P-212, P-280, P-318, P-319, P-419 and T-289 available from Chukyo Yushi Co., Ltd; and NCM9385 available from Sasol Corporation, and the like. If the releasing agent is a mixture of a paraffin-based wax and an ester-based wax, the amount of the ester-based wax may be in the range of about 5 to about 39 wt %, for example, about 7 to about 36 wt %, or about 9 to about 33 wt %, based on the total weight of the mixture. When the amount of the ester-based wax is greater than or equal to about 5 wt % based on the total weight of the mixture, the compatibility of the ester-based wax with a binder resin may be sufficiently maintained. When the amount of the ester-based wax is less than or equal to about 39 wt % based on the total weight of the mixture, toner may have appropriate plasticizing characteristics, and thus may retain satisfactory development characteristics for a long period of time.

[0044] In the toner according to examples of the present disclosure, compatibilization caused by trans-esterification, and/or other mechanism between the crystalline polyester and the amorphous polyester may be minimized by satisfying at least the conditions (1), (2), (3), and (4). Accordingly, a domain size and distribution of the releasing agent, a domain size and distribution of the crystalline binder resin, and a change in thermal properties of the toner may be appropriately adjusted in the toner particles. As a result, the toner may have sharp melting characteristics of the crystalline polyester and a high T_g of the amorphous polyester. Thus, the toner according to examples of the present disclosure may efficiently obtain stable durability due to wide fixing offset range, high fixing gloss, and good surface shapes of the toner particles. Thus, the toner according to examples of the present disclosure may have excellent low-temperature fixability, good surface characteristics of the toner particles, fluidity, charging stability, high-temperature storage ability, and durability against environmental changes. Thus, the toner according to examples of the present disclosure may have excellent properties such as high resolution, excellent durability, high gloss, low fixing temperature, and wide fusing latitude.

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[0045] Thermal and physical properties of polyester-based polymerization toner are affected by an inner morphological structure of toner particles which, in turn, is considerably affected by compatibility between components. Particularly, compatibility between the polyester binder resin and the releasing agent directly affects a domain size and dispersity of each component of the toner particles, and viscosity of the toner. Examples of factors related to the compatibility include interfacial tension, solubility parameter (SP), an average molecular weight, distribution of molecular weights, and acidic values. For example, when the solubility parameters between two components are similar, compatibility tends to be good, and thus this relationship may be used for designing a toner structure. For example, the solubility parameters of the binder resin and the releasing agent may be selected to form a combination which makes them an immiscible or partially miscible mixture. Furthermore, when a quantitative analysis result of the domain sizes and domain number of the releasing agent on a cross-section of the toner particle, and distribution of low molecular weight components are considered together, the possibility of plasticization may be predicted.

[0046] In this point of view, compatibilities between the amorphous polyester resin, the crystalline polyester resin, and the releasing agent of the toner according to examples of the present disclosure are adjusted to satisfy the following conditions (1) and (2).

$$1.0 \text{ (J/cm)}^{1/2} \leq \text{SP(A)} - \text{SP(C)} \leq 2.0 \text{ (J/cm)}^{1/2} \quad (1), \text{ and}$$

$$2.5 \text{ (J/cm)}^{1/2} \leq \text{SP(A)} - \text{SP(W)} \quad (2).$$

[0047] Wherein SP(A), SP(C), and SP(W) are solubility parameters (unit: $\text{(J/cm)}^{1/2}$) of the amorphous polyester resin, the crystalline polyester resin, and the releasing agent, respectively. Domains of the crystalline polyester resin and the releasing agent may be well formed by increasing the solubility parameter of the amorphous polyester resin to satisfy the conditions (1) and (2). As a result, the surface shape of the toner particle may be improved to inhibit the releasing agent from being exposed through the surface of the toner particle, thereby inhibiting excessive aggregation of toner particles and improving high-temperature storage ability, i.e., durability.

Rec

[0048] More particularly, the numerical range of the condition (1) may be about 1.2 to about 1.8, about 1.3 to about 1.7, about 1.4 to about 1.7, about 1.5 to about 1.7, or about 1.51 to about 1.65. The numerical range of the condition (2) may be, more particularly, about 2.6 or more, about 2.7 or more, about 2.8 or more, or about 2.9 or more.

[0049] Moreover, by decreasing the molecular weight of the amorphous polyester resin and increasing the molecular weight of the crystalline polyester resin to satisfy the conditions (5) and (7), a substantial difference between the solubility parameters of the both resins further increases, resulting in a decrease in compatibility between the two resins. Thus, domain formation of the crystalline polyester resin may be accelerated. As a result, the toner may have good surface shapes of the toner particles, wide fusing latitude, and high gloss:

$$2.5 \text{ kDa/wt\%} \leq \text{Mw(C)}/\text{Wt(C)} \leq 5.0 \text{ kDa/wt\%} \quad (5), \text{ and}$$

$$12.0 \text{ kDa} \leq \text{Mw(A)} \leq 25.0 \text{ kDa} \quad (7).$$

[0050] Wherein Mw(C) is a weight average molecular weight (unit: kDa) of the crystalline polyester resin measured by GPC performed on a THF-soluble fraction of the crystalline polyester resin, Wt(C) is a weight percentage (unit: wt%) of the crystalline polyester resin based on a total weight of the toner, and Mw(A) is a weight average molecular weight (unit: kDa) of the amorphous polyester resin measured by GPC performed on a THF-soluble fraction of the amorphous polyester resin.

[0051] By adjusting the solubility parameters of the releasing agent, the crystalline polyester resin, and the amorphous polyester resin to satisfy the conditions (3) and (4) during the preparation of the toner according to examples of the present disclosure, a releasing agent-crystalline polyester resin hybrid domain is formed due to a difference of compatibility therebetween. As a result, the melting point of the releasing agent and the melting point of the crystalline polyester resin are merged to have a single value. Thus, sharp melting of the toner becomes possible, and thus low-temperature fixability and gloss of the toner may be improved and the surface shapes of the toner particles may be enhanced:

$$\text{SP(C)} - \text{SP(W)} \leq 1.6 \text{ (J/cm)}^{1/2} \quad (3), \text{ and}$$

Rec

$$SP(C) - SP(W) \leq SP(A) - SP(C) \quad (4).$$

[0052] Wherein, SP(A), SP(C), and SP(W) are as defined above.

[0053] The numerical range of the condition (3) may be, more particularly, about 1.55 or less, about 1.50 or less, about 1.47 or less, about 1.45 or less, or about 1.40 or less.

[0054] By adjusting the difference of compatibility between the crystalline polyester resin and the releasing agent and the amount of the crystalline polyester resin, sizes and densities of microdomains inside the toner particle may significantly be changed. As the amount of the crystalline polyester resin decreases, the sizes of the domains and the degree of crystallization may decrease, resulting in a decrease in overall fixing rate. On the contrary, as the amount of the crystalline polyester resin is excessively large, low-temperature fixability and high-temperature storage ability may deteriorate. According to the preparation of the toner according to examples of the present disclosure, the weight average molecular weight Mw(C), the weight percentage Wt(C) based on the total weight of the toner, and the melting point Tm(C) of the crystalline polyester resin may be adjusted to satisfy the conditions (5) and (6). Thus, the low-temperature fixability, surface shape, and high-temperature storage ability of the toner may be improved.

$$2.5 \text{ kDa/wt\%} \leq Mw(C)/Wt(C) \leq 5.0 \text{ kDa/wt\%} \quad (5), \text{ and}$$

$$60 \text{ }^{\circ}\text{C} \leq Tm(C) \leq 90 \text{ }^{\circ}\text{C} \quad (6).$$

[0055] Wherein, Mw(C) is a weight average molecular weight (unit: kDa) of the crystalline polyester resin measured by GPC performed on a THF-soluble fraction, Wt(C) is a weight percentage (unit: wt%) of the crystalline polyester resin based on a total weight of the toner, and Tm(C) is a melting point (unit: °C) of the crystalline polyester.

[0056] The numerical range of the condition (5) may be about 3.0 to about 5.0, about 3.2 to about 5.0, about 3.4 to about 5.0, or about 3.2 to about 4.8 (unit: kDa/wt%).

Rec

[0057] The numerical range of the condition (6) may be about 60 °C to about 80 °C, about 62 °C to about 70 °C, about 64 °C to about 70 °C, about 65 °C to about 69 °C, or about 66 °C to about 69 °C.

[0058] Low-temperature fixability and surface shape, thus high-temperature storage ability of the toner may further be improved by adjusting the weight average molecular weight and the glass transition temperature of the amorphous polyester resin to satisfy the conditions (7) and (8) in the preparation of the toner according to examples of the present disclosure.

$$12.0 \text{ kDa} \leq \text{Mw(A)} \leq 25.0 \text{ kDa} \quad (7), \text{ and}$$

$$55 \text{ }^{\circ}\text{C} \leq \text{Tg(A)} \leq 70 \text{ }^{\circ}\text{C} \quad (8).$$

[0059] Wherein, Mw(A) is a weight average molecular weight (unit: kDa) of the amorphous polyester resin measured by GPC performed on a THF-soluble fraction, and Tg(C) is a glass transition temperature (unit: °C) of the amorphous polyester resin.

[0060] The numerical range of the condition (7) may be about 12.0 kDa to about 22.0 kDa, about 12.0 kDa to about 20.0 kDa, about 12.0 kDa to about 18.0 kDa, about 12.0 kDa to about 16.0 kDa, or about 12.0 kDa to about 15.0 kDa.

[0061] The numerical range of the condition (8) may be about 55 °C to about 70 °C, about 58 °C to about 68 °C, about 60 °C to about 68 °C, or about 62 °C to about 68 °C.

[0062] The toner having excellent low-temperature fixability, high gloss, and high high-temperature storage ability may be provided by strictly controlling compatibilities between components of the toner by adjusting the solubility parameters, the molecular weights, and the amounts of the polyester resins and the releasing agent used to prepare the core particles of the toner.

[0063] The toner may include iron (Fe), silicon (Si), and zinc (Zn), wherein the amounts of Si and Fe are each in the range of about 3 to about 1000 ppm, a molar ratio of Si to Fe (Si/Fe) is in the range of about 0.1 to about 5, and the [Si]/[Fe] ratio and the [Zn]/[Fe] ratio may satisfy the following conditions (9) and (10), wherein [Si], [Zn] and [Fe] denote the intensities of Si, Zn and Fe, respectively, as measured by X-ray fluorescence spectrometry:

Rec

$$0.0005 \leq [\text{Si}]/[\text{Fe}] \leq 0.05 \quad (9), \text{ and}$$

$$0.0005 \leq [\text{Zn}]/[\text{Fe}] \leq 0.5 \quad (10).$$

[0064] The intensity of zinc [Zn] is a value corresponding to the amount of zinc contained in a zinc-containing compound that is used as a catalyst in polymerizing the binder latex of the toner, i.e., the polyester resins. If [Zn] is too low, polymerization efficiency may be considerably low, and it may take longer to complete the reaction. On the other hand, if [Zn] is too large, the reaction rate may be too high to be controlled, and the molecular weight may be significantly increased so that the resulting toner may not be able to be appropriately fixed at low temperatures. Furthermore, if [Zn] is too large, the electrical characteristics of the final toner may be adversely affected. Thus, [Zn] is to be controlled within an appropriate range. The intensity of iron [Fe] is a value corresponding to the amount of Fe contained in an aggregating agent (or coagulant) that is used to aggregate the binder latex, the colorant and the releasing agent when toner is prepared. Thus, [Fe] may affect the aggregation properties, the particle size distribution and the particle size of aggregated toner. The intensity of silicon [Si] is a value corresponding to the amount of Si contained in an aggregating agent used for the toner or a silica external additive that is added to obtain the flowability of the toner. [Si] may affect properties of the toner like Fe, and may also affect flowability of the toner.

[0065] The ratio of [Zn] to [Fe], i.e., the [Zn]/[Fe] ratio may be from about 5.0×10^{-4} to about 5.0×10^{-3} , for example, from about 5.0×10^{-3} to about 5.0×10^{-2} . When the [Zn]/[Fe] ratio is within the range described above, appropriate aggregation rate and degree of aggregation may be obtained in the preparation of latex and excellent charging characteristics of the toner may be maintained.

[0066] The ratio of [Si] to [Fe], i.e., the [Si]/[Fe] ratio may be, for example, in the range of about 5.0×10^{-4} to about 5.0×10^{-2} , about 8.0×10^{-4} to about 3.0×10^{-2} , or about 1.0×10^{-3} to about 1.0×10^{-2} . When the [Si]/[Fe] ratio is within the range described above, the toner may have high flowability and the contamination of the internal components of the image forming apparatus in which the toner is employed may be suppressed.

Rec

[0067] The intensity of silicon [Si], the intensity of zinc [Zn], and the intensity of iron [Fe] may be measured by X-ray fluorescence spectrometry using an energy dispersive X-ray spectrometer (EDX-720) available from SHIMADZU Corporation. The measurement may be performed at an X-ray tube voltage of about 50 kV with a sample molding amount of $3 \text{ g} \pm 0.01 \text{ g}$. The ion intensity ratios $[\text{Zn}]/[\text{Fe}]$ and $[\text{Si}]/[\text{Fe}]$ of each sample may be calculated by using quantitative results of the intensities of silicon [Si], zinc [Zn], and iron [Fe] (unit: cps/ μA) obtained by the X-ray fluorescence measurement.

[0068] The core particles of the toner for developing electrostatic images according to examples of the present disclosure include a colorant. Examples of the colorant include a black colorant, a cyan colorant, a magenta colorant, a yellow colorant, or any combination thereof.

[0069] For example, the black colorant may be carbon black, aniline black, or a mixture thereof.

[0070] For example, the yellow colorant may be a condensed nitrogen compound, an isoindolelinone compound, an anthraquinone compound, an azo metal complex, an arylimide compound, or a mixture thereof. More particularly, examples of the yellow colorant include, but are not limited to, C.I. pigment yellows 12, 13, 14, 17, 62, 74, 83, 93, 94, 95, 109, 110, 111, 128, 129, 147, 168, and 180.

[0071] For example, the magenta colorant may be a condensed nitrogen compound, an anthraquinone compound, a quinacridone compound, a basic dye lake compound, a naphthol compound, a benzoimidazole compound, a thioindigo compound, a perylene compound, or a mixture thereof. More particularly, examples of the magenta colorant include, but are not limited to, C.I. pigment reds 2, 3, 5, 6, 7, 23, 48:2, 48:3, 48:4, 57:1, 81:1, 122, 144, 146, 166, 169, 177, 184, 185, 202, 206, 220, 221, and 254.

[0072] For example, the cyan colorant may be a copper phthalocyanine compound or a derivative thereof, an anthraquinone compound, a basic dye lake compound, or a mixture thereof. More particularly, examples of the cyan colorant include, but are not limited to, C.I. pigment blues 1, 7, 15, 15:1, 15:2, 15:3, 15:4, 60, 62, and 66.

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[0073] These colorants may be used alone or in combination of at least two thereof, and may be selected in consideration of color, chromaticity, brightness, weather resistance, or dispersibility in toner particles.

[0074] The amount of the colorant is not limited as long as it is sufficient to color the toner. For example, the amount of the colorant may be in the range of about 0.5 to about 15 parts by weight, about 1 to about 12 parts by weight, or about 2 to about 10 parts by weight, based on 100 parts by weight of the toner. When the amount of the colorant is about 0.5 parts by weight or above based on 100 parts by weight of the toner, a coloring effect may be satisfactorily shown. On the other hand, when the amount of the colorant is about 15 parts by weight or less, a preparation cost of the toner does not significantly increase, and a sufficient amount of charge may be provided.

[0075] The toner according to examples of the present disclosure may have a volume average particle diameter of about 3 to about 9 μm , for example, from about 4 to about 8 μm or from about 4.5 to about 7.5 μm . In general, the smaller the toner particle size, the higher the resolution and the higher the quality of an image that may be achieved. However, when transfer speed and cleansing force are taken into consideration, small toner particles may not be appropriate for all applications. Thus, it is better to have an appropriate toner particle size. The volume average diameter of the toner may be measured by electrical impedance analysis. When the volume average diameter is 3 μm or above, photoreceptor (or photoconductor) cleaning may be easily performed, a mass production yield may be improved, problems generated through scattering may be suppressed, and a high resolution and high quality image may be obtained. When the volume average diameter is 9 μm or lower, charging may be uniformly performed, fixability of the toner may be improved, and a doctor blade may easily control the toner layer on the photoreceptor.

[0076] An average circularity of the toner may be in the range of about 0.940 to about 0.980. For example, the average circularity may be in the range of about 0.945 to about 0.975, or about 0.950 to about 0.970. The average circularity may be calculated as follows. The average circularity may be in the range of 0 to 1, and as the average circularity approaches 1, the toner particle shape

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becomes more circular. When the toner has an average circularity of 0.940 or greater, an image developed on a transfer medium may have an appropriate thickness, and thus toner consumption may be reduced. In addition, voids between toner particles are not too large, and thus the image developed on the transfer medium may have a sufficient covering rate. On the other hand, when the toner has an average circularity of 0.980 or less, an excessive amount of toner being supplied onto a developer sleeve may be prevented, enabling to reduce the contamination of the developer sleeve that may result from the non-uniform coating of toner thereon.

[0077] The toner particle size distribution may be assessed using a volume average geometric size distribution coefficient (GSDv) or a number average geometric size distribution coefficient (GSDp). GSDv and GSDp of the toner according to examples of the present disclosure may be, respectively, about 1.3 or less and about 1.25 or less. The GSDv may be about 1.30 or less, for example, from about 1.15 to about 1.30. The GSDp may be about 1.25 or less, for example, from about 1.20 to about 1.25. When each of the GSDv and GSDp is within the above ranges, the toner may have a uniform particle diameter. A method of measuring the GSDv or GSDp will be described below.

[0078] According to an example, the shell layer is disposed or coated on the core particle. The shell layer includes the second binder resin including the amorphous polyester resin. The shell layer prevents crystalline materials, such as the crystalline polyester resin and the releasing agent, of the core particle that adversely affect the charging characteristics of the toner from being externally exposed, thereby increasing the charging stability and durability of the toner.

[0079] The toner for developing an electrostatic image according to examples of the present disclosure may be prepared by an aggregation method. The aggregation method may be performed by, for example, mixing a binder resin dispersion, a colorant dispersion, and a releasing agent dispersion; aggregating particles thereof; and fusing resultant aggregates. Particularly, the toner according to examples of the present disclosure may be prepared by an emulsion aggregation (EA) method suitable for precisely controlling particle size

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reduction and particle size distribution, besides controlling the compatibility of the crystalline and amorphous polyester resins and the releasing agent. Particularly, the toner according to examples of the present disclosure may be prepared to have a core-shell structure that stably forms a high quality image for a long period of time since the polymerization toner not only has excellent durability with respect to an environment, but also excellent color realization, low-temperature fixability, charging stability, and high-temperature storage characteristics. The toner according to examples of the present disclosure may be prepared by the EA method described below.

[0080] First, the polyester resin polymerized as described above is subjected to phase inversion emulsification to obtain a polyester latex having a latex particle size of about 100 nm to about 300 nm. The polyester latex may be obtained by dispersing a polyester resin, an alkaline compound, and optionally, a surfactant in an aqueous phase and subjecting the dispersion to phase inversion emulsification. A latex preparation process according to this method includes a dissolution/neutralization, an emulsification, and a solvent evaporation steps. In the dissolution/neutralization step, the polyester resin is dissolved in an organic solvent to prepare an organic polyester solution. A solvent capable of dissolving the polyester resin may be used as the organic solvent. In the emulsification step, the alkaline compound and water are added to the prepared resin solution to perform phase inversion emulsification. The surfactant may be added thereto. An amount of the alkaline compound may be determined to be equivalent to an amount of carboxylic acid groups obtained from an acid value of the polyester resin.

[0081] Next, the obtained polyester latex particles, a pigment dispersion, a releasing agent, and an aggregating agent are mixed, optionally with a homogenizer, and agitated. Then, primary aggregates corresponding to core particles are generated by shear-induced aggregation mechanism. The latex is further added thereto at a temperature of about 25 °C to about 70 °C (lower than T_g of the polyester resin), more particularly, about 35 °C to about 60 °C to form a shell layer on the core particle, and then a coalescence process is performed at a temperature of about 85 °C to about 100 °C (higher than the T_g

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by about 20 °C to about 50 °C). As a result, primary toner particles having a core/shell structure and a particle diameter of about 3 μm to about 9 μm, particularly about 5 μm to about 7 μm, may be obtained. The aggregating agent that may be used in the aggregation process may include polysilicato-iron compounds obtainable under the tradename of PSI-025, PS1-050, PSI-075, or PSI-100 available from SUIDO KIKO CO., LTD. The polysilicato-iron aggregating agent exhibits strong aggregating force even when used in a small amount at a low temperature. Moreover, since the polysilicato-iron aggregating agent includes iron and silicon as the main components, adverse effects of residual aluminum on the environment and human body caused when a trivalent polyaluminum aggregating agent is used, may be minimized.

[0082] An external additive may be attached to outer surfaces of the toner particles according to examples of the present disclosure. One of the main functions of the external additive is to maintain flowability of toner particles by preventing the toner particles from sticking together. Examples of the external additive that may be used include particles of silica, such as fumed silica or sol-gel silica, TiO₂ particles, and lanthanum strontium titanate (LaSrTiO₃) particles. The external additive may be attached to the surfaces of the toner particles, for example, by using a powder mixing apparatus. Examples of the powder mixing apparatus may be, but are not limited to, a Henshell mixer, a V-shape mixer, a ball mill, or a Nauta mixer.

[0083] Hereinafter, a toner supply device, an imaging apparatus, and a method of forming an image according to the present disclosure will be described.

[0084] The toner supply device includes the toner for developing electrostatic images according to the present disclosure. For example, the toner supply device includes: a toner tank in which toner may be stored; a supply part protruding from an inner surface of the toner tank to externally supply toner from the toner tank; and a toner-agitating member rotatably disposed inside the toner tank to agitate toner in the inner space of the toner tank comprising a space above a top surface of the supplying part. Here, the toner may be the toner according to the present disclosure.

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[0085] The imaging apparatus according to the present disclosure is an imaging apparatus including the toner for developing electrostatic images according to the present disclosure. For example, the imaging apparatus includes an image carrier; an image forming device configured to form an electrostatic image, for example, particularly an electrostatic latent image, on a surface of the image carrier; a toner storing device, such as the toner tank above, in which toner may be stored; a toner supplying device configured to supply the toner to the surface of the image carrier to develop the electrostatic image into a visible image on the surface of the image carrier; and a transferring device configured to transfer the visible image from the surface of the image carrier to an image receiving member, wherein the toner is the toner for developing electrostatic images according to the present disclosure.

[0086] The method of forming an image according to the present disclosure includes forming a visible image by attaching toner to a surface of an image carrier on which an electrostatic image is formed, and transferring the visible image to an image receiving member, e.g., a transfer medium, wherein the toner is the toner for developing electrostatic images according to the present disclosure. The method of forming an image may be carried out by an electrophotographic process. The electrophotographic process may include a charging step to uniformly charge the surface of an electrostatic image carrier, an exposure step to form an electrostatic image by using various photoconductive materials on the charged electrostatic image carrier, a developing step to develop a visible image (e.g., a toner image) by attaching a developer, such as toner, to the electrostatic image, a transferring step to transfer the visible image onto a transfer medium, such as paper, a cleaning step to remove toner that is not transferred and remains on the electrostatic image carrier, a charge eliminating step to remove charges remaining on the electrostatic image carrier, and a fixing step to fix the visible image by applying heat or pressure thereto. In this regard, the toner according to examples of the present disclosure may be efficiently used for an electrophotographic process, such as those described above.

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[0087] The present disclosure will now be described in detail with reference to the following examples and comparative examples. However, these examples and comparative examples are illustrative and are not intended to limit the scope of the present disclosure.

[0088] Examples

[0089] Physical properties of various polyester resins and releasing agents used in Examples 1 to 5 (sometimes abbreviated as E1 to E5) and Comparative Examples 1 to 9 (sometimes abbreviated as CE1 to CE9) are as shown in Table 1 below. Here, % refers to wt% unless otherwise stated below.

[0090] Glass transition temperatures T_g and melting points T_m of the amorphous polyester resins, the crystalline polyester resins, and the releasing agents shown in Table 1 are measured according to the methods described below. M_w denotes a weight average molecular weight of the polyester resins measured for THF-soluble fractions by GPC.

[0091] Table 1

	Solubility parameters (SP) [(J/cm ³) ^{0.5}]	Molecular weight (kDa)	T_g (°C)	T_m (°C)	Remarks
A1	11.36	14.4	63.5	-	Amorphous PES* resin (Kao Corporation, KUG-17/KUG-19 mixture)
A2	11.41	21.6	62.3	-	Amorphous PES resin (Kao Corporation, KUG-17/KUG-19 mixture)
A3	11.01	18.6	68.2	-	Amorphous PES resin (Kao Corporation, KUG-17/KUG-19 mixture)
A4	10.70	26.4	63.1	-	Amorphous PES resin (Kao Corporation, KUG-17/KUG-19 mixture)
A5	11.84	21.6	62.3	-	Amorphous PES resin (Kao Corporation, KUG-17/KUG-19 mixture)
C1	9.64	7.2	-	67.3	Crystalline PES resin (SK Chemicals, CPE-105)
C2	9.75	28.0	-	67.9	Crystalline PES resin (SK Chemicals, CPE-106)
C3	9.79	23.1	-	68.1	Crystalline PES resin (SK Chemicals, CPE-106)
C4	9.83	19.2	-	67.0	Crystalline PES resin (SK Chemicals, CPE-106)
C5	9.86	15.5	-	67.2	Crystalline PES resin

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					(SK Chemicals, CPE-106)
C6	9.67	13.5	-	66.3	Crystalline PES resin (SK Chemicals, CPE-106)
W1	8.37	-	-	72.4	Paraffin-based wax/ester-based wax mixture (Chukyo Yushi, Co., Ltd., T-289)
W2	8.61	-	-	69.1	Ester group-containing paraffin- based wax (Chukyo Yushi, Co., Ltd., P-787)
W3	8.06	-	-	73.6	Paraffin-based wax (Sasol Corporation, NCM9385)

* PES: polyester

[0092] Preparation Example 1**[0093]** Preparation of Latex A1 including Amorphous Polyester Resin A1

[0094] About 500 g of amorphous polyester resin A1, about 400 g of methyl ethyl ketone (MEK), and about 100 g of isopropyl alcohol (IPA) were added to a 3 L double-jacketed reactor, and the polyester resin A1 was dissolved at 30°C while stirring with an anchor-type mechanical stirrer to obtain a polyester resin solution. While agitating the obtained polyester resin solution, about 30 g of 10% aqueous ammonia solution was slowly added thereto. Then, while continuously agitating the solution, about 1,500 g of water was added thereto at a rate of about 50 g/min to prepare an emulsion. The solvent was removed from the prepared emulsion by distillation under reduced pressure to prepare Latex A1 having a solid content of about 25 %. A volume average particle diameter D50 of the prepared Latex A1 measured by a particle size analyzer (Microtrac Bluewave) was about 135 nm and GSDv was about 1.10. Throughout the specification, the volume average particle diameter D50 refers to a particle diameter at which the cumulative volume of the particles corresponds to 50 % of the total cumulative volume of the particles in a cumulative volume curve of the particles.

[0095] Preparation Example 2**[0096]** Preparation of Latex C1 including Crystalline Polyester Resin C1

[0097] About 500 g of crystalline polyester resin C1, about 400 g of MEK, and about 100 g of IPA were added to a 3 L double-jacketed reactor, and the polyester resin C1 was dissolved at about 60°C while stirring with an anchor-

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type mechanical stirrer to obtain a polyester resin solution. While agitating the obtained polyester resin solution, about 30 g of 10% aqueous ammonia solution was slowly added thereto. Then, while continuously agitating the solution, about 1,500 g of water was added thereto at a rate of about 50 g/min to prepare an emulsion. The solvent was removed from the prepared emulsion by distillation under reduced pressure to prepare Latex C1 having a solid content of about 25 %. A volume average particle diameter D50 of the prepared Latex C1 measured by a particle size analyzer (Microtrac Bluewave) was about 140 nm and GSDv was about 1.11.

[0098] Preparation Example 3**[0099]** Preparation of Colorant Dispersion

[00100] About 10 g of an anionic reactive emulsifier (HS-10; Daiichi Kogyo Seiyaku Co., Ltd.) and about 60 g of a cyan pigment (PB 15:4) were loaded into a milling bath and then, about 400 g of glass beads having a diameter of about 0.8 mm to about 1 mm were added thereto. The mixture was milled at room temperature to prepare a colorant dispersion. A homogenizer used in this experiment was an ultrasonic homogenizer or a micro fluidizer.

[00101] Releasing Agent Dispersion

[00102] Wax dispersions purchased from Chukyo Yushi, Co., Ltd. shown in Table 1 were used.

[00103] Example 1**[00104]** Aggregation and Preparation of Toner

[00105] About 316 g of deionized water, about 250 g of Latex A1, and 57 g of Latex C2 were added to a 1 L reactor and the mixture was agitated at about 350 rpm. About 35 g of the cyan pigment dispersion (HS-10 100%) prepared in Preparation Example 3, and about 28 g of a wax dispersion P-419 (Chukyo Yushi, Co., Ltd.) were added to the reactor. Then, about 30 g (0.3 mol) of 0.3 N nitric acid and about 15 g of 12 % PSI-100 (SUIDO KIKO CO., LTD.) as an aggregating agent were added thereto and the mixture was agitated by using a

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homogenizer at about 11,000 rpm for about 6 minutes while gradually heating up to about 45 °C to prepare miniature toner having a volume average particle diameter D50 of about 0.5 µm to about 3 µm. Then, aggregation is further performed for about 2 hours to obtain primary toner aggregates having a volume average particle diameter of about 4 µm to about 5 µm.

[00106] Next, about 150 g of Latex A2 prepared for a shell layer was added to the reactor. When a volume average particle diameter of Latex A2 reached about 5 µm to about 6 µm, NaOH (1 mol) was added to adjust the pH to about 7. When the volume average particle diameter D50 is maintained constant for about 10 minutes, the reactor was heated to about 95 °C at a rate of 0.5 °C/min. After reaching about 95 °C, nitric acid (0.3 mol) was added thereto to adjust the pH to about 5.7 and the mixture was fused for about 4 hours to about 5 hours to obtain a secondary aggregated toner having a potato shape with a volume average particle diameter of about 5.5 µm to about 6.5 µm. Then, the aggregated reaction solution was cooled to a temperature lower than T_g, and then was filtered to isolate toner particles, followed by drying.

[00107] About 100 g of the dried toner particles, about 0.5 g of silica particles NX-90 (Nippon Aerosil), about 1.0 g of silica particles RX-200 (Nippon Aerosil), and about 0.5 g of titanium dioxide particles SW-100 (Titan Industry Co. LTD.) were put into a mixer (KM-LS2K, available from DAE WHA Tech Co., Ltd.) and the mixture was agitated at about 8,000 rpm for 4 minutes to add an external additive to the toner particles. The resultant toner had a volume average particle diameter of about 5.5 µm to about 6.0 µm. The resultant toner had GSD_v and GSD_p of about 1.22 and about 1.23, respectively, and an average circularity of the resultant toner was 0.972.

[00108] Examples 2 to 5 and Comparative Examples 1 to 9

[00109] Aggregation and Preparation of Toner

[00110] Toner particles were prepared according to Examples 2 to 5 and Comparative Examples 1 to 9 in the same manner as in Example 1, except that types of the crystalline polyester resin, the amorphous polyester resin, and the releasing agent for core particles were changed as shown in Table 2 below. The

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crystalline polyester resin latexes, amorphous polyester resin latexes, and releasing agent dispersions that were used herein were prepared according to the method described above with reference to Preparation Examples 1 to 3.

[00111] Various physical properties of the toners prepared according to Examples 1 to 5 and Comparative Examples 1 to 9 are shown in Table 2 below.

Table 2

	*E 1	E 2	E 3	E 4	E 5	*CE 1	CE 2	CE 3	CE 4	CE 5	CE 6	CE 7	CE 8	CE 9
Resin1	A1	A1	A1	A1	A1	A1	A2	A1	A3	A3	A4	A4	A5	A5
Resin2	C2	C3	C3	C4	C2	C4	C1	C5	C5	C5	C6	C6	C1	C1
Releasing agent	W1	W1	W1	W1	W1	W1	W1	W1	W1	W1	W2	W2	W3	W3
Condition (1)	1.61	1.57	1.57	1.53	1.61	1.53	1.77	1.50	1.14	1.14	1.03	1.03	2.20	2.20
Condition (2)	2.99	2.99	2.99	2.99	2.99	2.99	3.04	2.99	2.60	2.60	2.22	2.22	3.78	3.78
Condition (3)	1.38	1.42	1.42	1.46	1.38	1.46	1.27	1.49	1.49	1.49	1.30	1.30	1.58	1.58
Condition (4)	3.50	4.60	3.29	4.75	4.67	3.17	1.10	2.50	3.33	2.50	2.70	1.93	0.83	1.10
Cold Offset Temperature (°C)	150	150	150	155	150	155	160	155	160	160	165	160	150	155
Hot Offset Temperature (°C)	190	190	200	185	200	180	180	175	190	185	190	185	190	195
Gloss	11.4	11.5	11.8	10.8	10.0	11.0	10.0	12.5	10.5	10.6	10.1	10.9	12.3	11.6
#SC	○	◎	△	○	◎	○	○	○	×	△	×	×	×	△
#HTSA	◎	◎	◎	○	◎	△	◎	×	△	×	△	×	×	△
Flowability	◎	◎	◎	○	◎	○	◎	△	○	△	△	△	△	○

* E: Example, CE: Comparative Example

SC: Surface characteristics, #: HTSA: High-temperature storage ability

[00112] Various physical properties of the toners prepared according to Examples 1 to 5 and Comparative Examples 1 to 9 were evaluated using the following evaluation methods.

[00113] Methods of Evaluating Toner

[00114] < Evaluation of Average Circularity >

[00115] The toner particle shape is checked by using a scanning electron microscope (SEM). The circularity of toner may be measured using a flow particle image analyzer (e.g., the FPIA-3000 particle analyzer available from SYSMEX Corporation of Kobe, Japan), and using the following equation:

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$$\text{Circularity} = 2 \times (\pi \times \text{area})^{0.5} / \text{circumference} \quad \dots \text{Equation.}$$

The circularity may be in the range of 0 to 1, and as the circularity approaches 1, the toner particle shape becomes more circular. Average circularity is obtained by calculating an average circularity of 3,000 toner particles.

[00116] <Evaluation of Particle Size Distribution>

[00117] GSDv and GSDp, which are measures of geometric size distribution of toner particles, are measured by using Multisizer III (manufactured by Beckman Coulter), which is a Coulter counter, under the following conditions.

Electrolyte: ISOTON II

Aperture Tube: 100 μm

Number of Measured Particles: 30,000.

[00118] Geometric size distribution of the toner is then divided into predetermined particle diameter ranges (channels). With respect to the respective particle diameter ranges (channels), the cumulative volume distribution of toner particles and the cumulative number distribution of toner particles are produced, wherein, in each of the cumulative volume and number distributions, the particle size in each distribution is increased in a direction from left to right. A cumulative particle diameter at 16% of the respective cumulative distributions is defined as a volume average diameter D16v and a number average particle diameter D16p. Likewise, a cumulative particle diameter at 84% of the respective cumulative distributions is defined as a volume average diameter D84v and a number average particle diameter D84p. GSDv and GSDp are calculated as follows:

$$\text{GSDv} = (\text{D84v}/\text{D16v})^{0.5},$$

$$\text{GSDp} = (\text{D84p}/\text{D16p})^{0.5}.$$

[00119] <Measurement of Glass Transition Temperature and Melting Temperature>

[00120] A DSC curve is obtained under the following heat profile, with respect to 6 to 7 mg samples in powder shape under a nitrogen gas atmosphere, by using Perkin Elmer DSC6 device.

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- Primary Heating: from room temperature to 150 °C at a rate of 10 °C/min, and maintained at a temperature of 150 °C for 1 minute,
- Cooling: from 150 °C to 0 °C at a rate of -10 °C/min and maintained at a temperature of 0 °C for 1 minute,
- Secondary Heating: from 0 °C to 150 °C at a rate of 10 °C/min.

[00121] Melting temperatures of the crystalline polyester resin and the releasing agent are determined based on a vertex of an endothermic peak showing a crystalline melting on the DSC curve. Also, glass transition temperature of the amorphous polyester is determined based on a half Cp value of a shoulder type curve indicating a baseline shift showing a glass transition phenomenon.

[00122] <Evaluation of Toner Fixability>

[00123] An NIF-type fixing device which is the same fixing device as that is installed in SL-X7600 laser printer available from Samsung Electronics Co., Ltd. is used to fix a test image under the following conditions.

- Unfixed Image for Testing: 100% Pattern
- Test Temperature: from 100 °C to 200 °C (at an interval of 10 °C)
- Test Paper: 60 g paper sheet (X-9 available from Boise, Inc.), and 90 g paper sheet (Xerox Exclusive Available from Xerox Corp)
- Fixing Speed: 160 mm/sec
- Dwell Time: 0.08 sec.

[00124] The fixability of the fixed image is measured as follows: The optical density (OD) of the fixed image is measured, and then a 3M 810 tape is attached to the fixed image. A weight of 500 g is reciprocated thereon five times, and then the tape used is removed. Then, the OD of the fixed image is measured again.

(1) The fixability is evaluated according to following equation:

$$\text{Fixability (\%)} = (\text{OD after peeling off the tape}) / (\text{OD before peeling off the tape}) \times 100$$

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A fixing temperature range in which the fixability is 90% or more is defined as the fusing latitude of toner.

(2) The minimum temperature at which the fixability is 90% or more without a cold-offset phenomenon is regarded as a cold-offset temperature (COT).

(3) The minimum temperature at which a hot-offset phenomenon occurs is regarded as a hot-offset temperature (HOT).

[00125] <Evaluation of Gloss>

[00126] Gloss (%) is measured using a glossmeter (Product Name: micro-TRI-gloss available from BYK-Gardner) at a temperature of 167 °C at which the fixing device is used.

- Measurement Angle: 60°,
- Measurement Pattern: 100% Pattern.

[00127] <Evaluation of Surface Characteristics of Toner>

[00128] Several mg of dry toner is observed to evaluate surface states (i.e., surface characteristics) of toner by using a scanning electron microscope. Surface characteristics is evaluated based on the following criteria.

- Evaluation Criteria

- ◎: Excellent surface shape, no releasing agent protruding portion and no surface voids
- : Good surface shape, very few surface voids
- △: Slightly rough surface shape, very few releasing agent protruding portions and surface voids
- X: Very poor surface shape, many releasing agent protruding portions and many surface voids. Damages on surfaces of toner particles are observed.

[00129] <Evaluation of High-Temperature Storage Ability>

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[00130] 100 g of externally added toners are added to a developing unit which is the same developing unit as that is installed in the SL-X7600 laser printer and stored under the following conditions in a constant-temperature and constant-humidity oven while being packed.

=> 23 °C, 55% RH (Relative Humidity), 2 hours

=> 40 °C, 90% RH, 48 hours

=> 50 °C, 80% RH, 48 hours

=> 40 °C, 90% RH, 48 hours

=> 23 °C, 55% RH, 6 hours.

[00131] After storing under the conditions described above, it is identified with the naked eye whether toner caking occurs in the developing unit, and a 100% pattern image is output to evaluate image defects.

- Evaluation Criteria

◎: Excellent image, excellent flowability

○: Good image, no caking

△: Poor image, no caking

X: Caking occurred.

[00132] <Evaluation of Flowability of Toner>

[00133] Cohesiveness is measured as follows to evaluate flowability of the toner.

Equipment: Hosokawa micron powder tester PT-S

Amount of sample: 2 g

Amplitude: 1 mm dial 3 to 3.5

Sieves: 53 µm, 45 µm, and 38 µm

Vibration time: 120±0.1 seconds

After the toner samples are stored for 2 hours under the conditions of room temperature (20°C±2 °C) and relative humidity of 55±5%, the samples are sieved using each sieve under the above conditions, and changes in amount of the toner before and after sieving are measured to calculate the cohesiveness of the toner as follows.

(1) [mass of powders remaining on 53 µm sieve/2 g]x100

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(2) [mass of powders remaining on 45 μm sieve/2 g] $\times 100 \times (3/5)$

(3) [mass of powders remaining on 38 μm sieve/2 g] $\times 100 \times (1/5)$

Degree of cohesiveness (Carr's cohesion) = (1)+(2)+(3).

The flowability of the toner is evaluated from the degree of cohesiveness measured as above according to the following criteria.

◎: degree of cohesiveness of 10 or less (Very good flowability)

○: degree of cohesiveness of greater than 10 to 15 (good flowability)

△: degree of cohesiveness of greater than 15 to 20 (little poor flowability)

×: degree of cohesiveness of greater than 20 (very poor flowability)

[00134] Referring to Table 2, it can be seen that the toners according to Examples 1 to 5 have excellent low-temperature fixability due to low COT, wide fixing latitude defined by a difference between COT and HOT, high gloss, excellent surface characteristics of the toner, excellent high-temperature storage ability, and high flowability by controlling the components to satisfy Conditions (1), (2), (3) and (4) in comparison with the toners according to Comparative Examples 1 to 9. Particularly, the toners according to Examples 1 to 5 have wider fixing latitude and better low-temperature fixability, surface characteristics, high-temperature storage ability, and flowability than the toners according to Comparative Examples 1 to 9.

[00135] It is believed that these results are obtained since the domain size and distribution of the releasing agent, the domain size and distribution of the crystalline binder resin, and the change in thermal properties in toner particles are strictly controlled by controlling compatibilities among the components of the toner through adjustment of the difference of solubility parameters between the polyester resins and the releasing agent, the molecular weights and molecular weight distribution of the polyester resins, and amounts of the polyester resins.

[00136] While examples have been described with reference to the figures, it will be understood by those of ordinary skill in the art that various changes in form and details may be made therein without departing from the spirit and scope as defined by the following claims.

WHAT IS CLAIMED IS:

1. A toner for developing electrostatic images, comprising:

a plurality of toner particles,

wherein each toner particle of the plurality of toner particles includes:

a core particle including a first binder resin, a colorant, and a releasing agent; and

a shell layer coating the core particle, the shell layer including a second binder resin,

the first binder resin of the core particle comprises about 80 wt% or more of a first amorphous polyester resin and about 20 wt% or less of a crystalline polyester resin, based on a total weight of the first binder resin,

the second binder resin comprises a second amorphous polyester resin,

the first amorphous polyester resin has a solubility parameter $SP(A)$ $((J/cm)^{1/2})$,

the crystalline polyester resin has a solubility parameter $SP(C)$ $((J/cm)^{1/2})$,

the releasing agent has solubility parameters $((J/cm)^{1/2})$, and

$SP(A)$, $SP(C)$, and $SP(W)$ satisfy following conditions (1), (2), (3), and (4):

$$1.0 (J/cm)^{1/2} \leq SP(A) - SP(C) \leq 2.0 (J/cm)^{1/2} \quad (1),$$

$$2.5 (J/cm)^{1/2} \leq SP(A) - SP(W) \quad (2),$$

$$SP(C) - SP(W) \leq 1.6 (J/cm)^{1/2} \quad (3), \text{ and}$$

$$SP(C) - SP(W) \leq SP(A) - SP(C) \quad (4).$$

2. The toner of claim 1, wherein

the crystalline polyester resin has a weight average molecular weight $Mw(C)$ (unit: kiloDalton (kDa)), a weight percentage $Wt(C)$ (unit: wt%) based on a total weight of the toner, and a melting point $Tm(C)$ (unit: °C), and

the weight average molecular weight $Mw(C)$ (unit: kiloDalton (kDa)), the weight percentage $Wt(C)$ (unit: wt%) based on the total weight of the toner, and the melting point $Tm(C)$ (unit: °C) of the crystalline polyester resin satisfy the following conditions (5) and (6):

$$2.5 \text{ kDa/wt\%} \leq Mw(C)/Wt(C) \leq 5.0 \text{ kDa/wt\%} \quad (5), \text{ and}$$

$$60\text{ }^{\circ}\text{C} \leq T_m(C) \leq 90\text{ }^{\circ}\text{C} \quad (6),$$

where $M_w(C)$ is measured by gel permeation chromatography (GPC) performed on a tetrahydrofuran (THF)-soluble fraction of the crystalline polyester resin.

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3. The toner of claim 2, wherein

the first amorphous polyester resin has a weight average molecular weight $M_w(A)$ (unit: kDa) and a glass transition temperature $T_g(A)$ (unit: $^{\circ}\text{C}$), and

the weight average molecular weight $M_w(A)$ (unit: kDa) and the glass transition temperature $T_g(A)$ (unit: $^{\circ}\text{C}$) of the first amorphous polyester resin satisfy following conditions (7) and (8):

10

$$12.0\text{ kDa} \leq M_w(A) \leq 25.0\text{ kDa} \quad (7), \text{ and}$$

$$55\text{ }^{\circ}\text{C} \leq T_g(A) \leq 70\text{ }^{\circ}\text{C} \quad (8),$$

where $M_w(A)$ is measured by GPC performed on a THF-soluble fraction of the first amorphous polyester resin.

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4. The toner of claim 1, wherein the releasing agent comprises at least one selected from a polyethylene-based wax, a polypropylene-based wax, a silicone-based wax, a paraffin-based wax, an ester-based wax, a carnauba-based wax, and a metallocene-based wax.

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5. The toner of claim 1, wherein a volume average particle diameter of the plurality of toner particles of the toner is from about 3 μm to about 9 μm .

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6. The toner of claim 1, wherein an average circularity of the plurality of toner particles of the toner is from about 0.940 to about 0.980.

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7. The toner of claim 1, wherein a volume average geometric size distribution coefficient (GSDv) and a number average geometric size distribution coefficient (GSDp) of the plurality of toner particles of the toner are about 1.30 or less and about 1.25 or less, respectively.

8. A toner supply device comprising:
a toner for developing electrostatic images, the toner including a plurality of toner particles,

wherein each toner particle of the plurality of toner particles includes:
a core particle including a first binder resin, a colorant, and a releasing agent; and

a shell layer coating the core particle, the shell layer including a second binder resin,

the first binder resin of the core particle comprises about 80 wt% or more of a first amorphous polyester resin and about 20 wt% or less of a crystalline polyester resin, based on a total weight of the first binder resin,

the second binder resin comprises a second amorphous polyester resin,
the first amorphous polyester resin has a solubility parameter $SP(A)$ $((J/cm)^{1/2})$,
the crystalline polyester resin has a solubility parameter $SP(C)$ $((J/cm)^{1/2})$,
the releasing agent has solubility parameters $((J/cm)^{1/2})$, and
 $SP(A)$, $SP(C)$, and $SP(W)$ satisfy following conditions (1), (2), (3), and (4):

$$1.0 (J/cm)^{1/2} \leq SP(A) - SP(C) \leq 2.0 (J/cm)^{1/2} \quad (1),$$

$$2.5 (J/cm)^{1/2} \leq SP(A) - SP(W) \quad (2),$$

$$SP(C) - SP(W) \leq 1.6 (J/cm)^{1/2} \quad (3), \text{ and}$$

$$SP(C) - SP(W) \leq SP(A) - SP(C) \quad (4).$$

9. The toner supply device of claim 8, comprising:
a toner tank in which toner is stored;
a supply part protruding from an inner surface of the toner tank to externally supply the toner from the toner tank; and
a toner-agitating member rotatably disposed inside the toner tank to agitate the toner in the toner tank comprising a space above a top surface of the supplying part.

10. An imaging apparatus comprising:

a toner storing device including a toner for developing electrostatic images, the toner including a plurality of toner particles,

wherein each toner particle of the plurality of toner particles includes:

a core particle including a first binder resin, a colorant, and a releasing agent; and

a shell layer coating the core particle, the shell layer including a second binder resin,

the first binder resin of the core particle comprises about 80 wt% or more of a first amorphous polyester resin and about 20 wt% or less of a crystalline polyester resin, based on a total weight of the first binder resin,

the second binder resin comprises a second amorphous polyester resin,

the first amorphous polyester resin has a solubility parameter $SP(A)$ $((J/cm)^{1/2})$,

the crystalline polyester resin has a solubility parameter $SP(C)$ $((J/cm)^{1/2})$,

the releasing agent has solubility parameters $((J/cm)^{1/2})$, and

$SP(A)$, $SP(C)$, and $SP(W)$ satisfy following conditions (1), (2), (3), and (4):

$$1.0 (J/cm)^{1/2} \leq SP(A) - SP(C) \leq 2.0 (J/cm)^{1/2} \quad (1),$$

$$2.5 (J/cm)^{1/2} \leq SP(A) - SP(W) \quad (2),$$

$$SP(C) - SP(W) \leq 1.6 (J/cm)^{1/2} \quad (3), \text{ and}$$

$$SP(C) - SP(W) \leq SP(A) - SP(C) \quad (4).$$

11. The imaging apparatus of claim 10, wherein the imaging apparatus comprises:

an image carrier;

an image forming device to form an electrostatic image on a surface of the image carrier;

a toner supplying device to supply the toner from the toner storing device to the surface of the image carrier to develop the electrostatic image into a visible image on the surface of the image carrier; and

a transferring device to transfer the visible image from the surface of the image carrier to an image receiving member.

12. The toner supply device of claim 8, wherein
the crystalline polyester resin has a weight average molecular weight $M_w(C)$ (unit: kiloDalton (kDa)), a weight percentage $Wt(C)$ (unit: wt%) based on a total weight of the toner, and a melting point $T_m(C)$ (unit: °C), and

5 the weight average molecular weight $M_w(C)$ (unit: kiloDalton (kDa)), the weight percentage $Wt(C)$ (unit: wt%) based on the total weight of the toner, and the melting point $T_m(C)$ (unit: °C) of the crystalline polyester resin satisfy the following conditions (5) and (6):

$$2.5 \text{ kDa/wt\%} \leq M_w(C)/Wt(C) \leq 5.0 \text{ kDa/wt\%} \quad (5), \text{ and}$$

$$60 \text{ }^\circ\text{C} \leq T_m(C) \leq 90 \text{ }^\circ\text{C} \quad (6),$$

10 where $M_w(C)$ is measured by gel permeation chromatography (GPC) performed on a tetrahydrofuran (THF)-soluble fraction of the crystalline polyester resin.

15 13. The toner supply device of claim 8, wherein
the first amorphous polyester resin has a weight average molecular weight $M_w(A)$ (unit: kDa) and a glass transition temperature $T_g(A)$ (unit: °C), and
the weight average molecular weight $M_w(A)$ (unit: kDa) and the glass transition temperature $T_g(A)$ (unit: °C) of the first amorphous polyester resin satisfy following
20 conditions (7) and (8):

$$12.0 \text{ kDa} \leq M_w(A) \leq 25.0 \text{ kDa} \quad (7), \text{ and}$$

$$55 \text{ }^\circ\text{C} \leq T_g(A) \leq 70 \text{ }^\circ\text{C} \quad (8),$$

25 where $M_w(A)$ is measured by GPC performed on a THF-soluble fraction of the first amorphous polyester resin.

14. The toner supply device of claim 8, wherein
a volume average particle diameter of the plurality of toner particles of the toner is from about 3 μm to about 9 μm , and
a volume average geometric size distribution coefficient (GSDv) and a number
30 average geometric size distribution coefficient (GSDp) of the plurality of toner particles of the toner are about 1.30 or less and about 1.25 or less, respectively.

15. The imaging apparatus of claim 10, wherein
the crystalline polyester resin has a weight average molecular weight $M_w(C)$
(unit: kiloDalton (kDa)), a weight percentage $Wt(C)$ (unit: wt%) based on a total weight
5 of the toner, and a melting point $T_m(C)$ (unit: °C), and
the weight average molecular weight $M_w(C)$ (unit: kiloDalton (kDa)), the weight
percentage $Wt(C)$ (unit: wt%) based on the total weight of the toner, and the melting
point $T_m(C)$ (unit: °C) of the crystalline polyester resin satisfy the following conditions (5)
and (6):

10
$$2.5 \text{ kDa/wt\%} \leq M_w(C)/Wt(C) \leq 5.0 \text{ kDa/wt\%} \quad (5), \text{ and}$$

$$60 \text{ }^\circ\text{C} \leq T_m(C) \leq 90 \text{ }^\circ\text{C} \quad (6),$$

where $M_w(C)$ is measured by gel permeation chromatography (GPC)
performed on a tetrahydrofuran (THF)-soluble fraction of the crystalline polyester
resin.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 2019/027295

A. CLASSIFICATION OF SUBJECT MATTER <i>G03G 9/08 (2006.01)</i> <i>G03G 9/087 (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)		
G03G 5/00, G03G 9/00, G03G 9/087, G03G 9/09, G03G 9/10, G03G 9/13, G03G 15/00, G03G 15/01-15/22, C09D 11/00-11/107		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
PatSearch (RUPTO internal), USPTO, PAJ, Esp@cenet, DWPI, EAPATIS, PATENTSCOPE, Information Retrieval System of FIPS		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 8431307 B2 (SAMSUNG ELECTRONICS CO., LTD) 30.04.2013	1-15
A	US 8642239 B2 (SAMSUNG ELECTRONICS CO., LTD.) 04.02.2014	1-15
A	EP 1930781 A2 (FUDJI XEROX CO., LTD.) 11.06.2008	1-15
A	US 20160259259 A1 (KONICA MINOLTA, INC) 08.09.2016	1-15
☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
*	Special categories of cited documents:	“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
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“P”	document published prior to the international filing date but later than the priority date claimed	
Date of the actual completion of the international search		Date of mailing of the international search report
15 July 2019 (15.07.2019)		08 August 2019 (08.08.2019)
Name and mailing address of the ISA/RU: Federal Institute of Industrial Property, Berezhkovskaya nab., 30-1, Moscow, G-59, GSP-3, Russia, 125993 Facsimile No: (8-495) 531-63-18, (8-499) 243-33-37		Authorized officer E. Panferova Telephone No. (499) 240-25-91