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(54) Toner and process cartridge using the toner

(57) A toner including a binder resin, a colorant, a release agent including a paraffin wax having a melting point of from 60 to 90 ˚C, and an inorganic filler including a montmorillonite or modified montmorillonite. The toner has a circularity of not less than 0.94, a thermal property such that when the toner is subjected to a differentials-canning calorimetric(DSC) analysis, the endothermic quantity calculated by the endothermic peak specific to the release agent is from 3. 0 to 6. 0 J/g, and a fluidity such that when a cone-shaped rotor is entered into a toner layer by 20 mm at an entering speed of 5 mm /sec, the torque generated by the toner is from 1.4 to 2.0 mNm. A process cartridge including an image bearing member configured to bear an electrostatic image and a developing device configured to develop the electrostatic image using the toner.

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Description

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] The present invention relates to a toner for use in developing an electrostatic image. In addition, the present invention also relates to a process cartridge, which forms visual images using the toner.

Discussion of the Background

[0002] Recently, a need exists for an electrophotographic image forming apparatus which can produce high quality images. In attempting to fulfill the need, various electrophotographic image forming apparatuses and toners have been proposed and developed. In order to produce high quality images with a toner, the toner preferably has a sharp particle diameter distribution. Specifically, when a toner has a sharp particle diameter distribution, the particles of the toner can exhibit almost the same behavior in an image developing process, and thereby images with improved fine dot reproducibility can be produced. Recently, toner produced by a granulation method (this toner is hereinafter sometimes referred to as a granulized toner) attracts attention because of having a sharp particle diameter distribution unlike conventional pulverization/classification toners which are prepared by kneading toner constituents, pulverizing the kneaded toner constituents, and then classifying the pulverized mixture of the toner constituents, resulting in formation of toner particles. Specific examples of the granulation methods include suspension polymerization methods, emulsion polymerization methods, and solution suspension methods in which a solution (or dispersion) including toner constituents (such as binder resins and colorants) is dispersed in a liquid to prepare toner particles in the liquid. Among these granulation methods, emulsion polymerization methods and solution suspension methods can relatively easily control the shape of the toner particles.

[0003] In order to prepare a spherical toner by a pulverization/classification method, published examined Japanese patent application No. 04-027897 and published unexamined Japanese patent application No. (hereinafter referred to as JP-A) 06-317928 have disclosed a technique in that a toner prepared by a pulverization/classification method is subjected to a heat treatment to prepare spherical toner particles. Further, in order to prepare a small spherical toner, which can produce high quality images and which has a good transferability, JP-A 01-257857 discloses a technique in that a spherical toner is prepared in a liquid by a granulation method such as suspension polymerization methods, emulsion polymerization methods and solution suspension methods.

[0004] When a toner has a sharp particle diameter distribution, the particles of the toner can exhibit almost the same behavior in an image developing process, and thereby images with improved fine dot reproducibility can be produced. However, conventional toners having a relatively small particle diameter and a relatively sharp particle diameter distribution tend to cause a cleaning problem in that toner particles remaining on the surface of an image bearing member (such as photoreceptors and intermediate transfer belts) cannot be well removed with a cleaning blade, resulting in formation of images with background development. This is because such toner particles easily pass through the nip between the surface of the image bearing member and the tip of the cleaning blade.

[0005] In attempting to solve the cleaning problem on the toner side, various proposals have been made. For example, a toner whose particle form is changed from the spherical form to irregular forms (this particle-form change is hereinafter sometimes referred to as deformation) is proposed. By deforming a toner, the fluidity of the toner deteriorates and thereby toner particles remaining on an image bearing member can be relatively easily blocked with a cleaning blade. Therefore, the residual toner particles can be well removed with the blade. However, when deformation of a toner is excessively performed, the behavior of the toner particles thereof becomes unstable in a developing process, resulting in deterioration of the fine dot reproducibility of the toner.

[0006] In addition, by deforming particles of a toner so as to have asperities, an external additive (such as silica), which is mixed with the toner particles to improve the fluidity thereof, is weakly adhered to the toner particles particularly at recessed portions of the toner particles, and thereby the external additive tends to be released from the toner particles. Therefore, a toner adhesion problem in that the toner particles are adhered to image bearing members (such as photoreceptors), fixing rollers and carrier particles occurs, resulting in formation of abnormal images.

[0007] In addition, by deforming particles of a toner, the cleanability of the toner is improved, but the fixability of the toner tends to deteriorate. Specifically, when particles of a toner are deformed, the toner layer constituting a toner image has low packing density (because there are many voids in the toner layer), and therefore the toner layer has low heat conductivity, resulting in deterioration of the low temperature fixability of the toner. This phenomenon is remarkable when the fixing pressure is relatively low.

[0008] Published unexamined Japanese patent application No. (hereinafter referred to as JP-A) 11-133665 discloses a toner constituted of a polyester resin and having a Wadell working sphericity of from 0.90 to 1.00. This toner has

substantially spherical form, and therefore the toner has poor cleanability.

[0009] In attempting to improve the low temperature fixability of toner, techniques in that polyester resins, which have a relatively good combination of low temperature fixability and high temperature preservability compared to styrene - acrylic resins conventionally used as binder resins, are used as binder resins thereof have been proposed. In attempting to further improve the low temperature fixability, the thermal properties of the binder resins have to be controlled. In this regard, for example, when a resin having too low a glass transition temperature (Tg) is used as the binder resin, the high temperature preservability of the toner deteriorates. When the molecular weight of the binder resin is excessively decreased to lower the softening point (T(F1/2)), a problem which occurs is that the hot offset temperature, at which a hot offset phenomenon is caused, seriously decreases. Thus, even when polyester resins, which have good low temperature fixability, are used as binder resins, toner having a good combination of low temperature fixability and hot offset resistance has not yet been prepared because the thermal properties of the binder resins are not controlled.

[0010] In addition, controlling the thermal properties of a binder resin to improve the low temperature fixability of the resultant toner often causes a problem in that the release agent and/or the polyester resin having a relatively low melting point, which are included in the toner, are adhered to carrier particles used for frictionally charging the toner after the toner is repeatedly used while agitated in a developing device, thereby deteriorating the charging ability of the carrier particles, resulting in decrease of the charge quantity of the toner and deterioration of image qualities.

[0011] The solution suspension methods have an advantage such that polyester resins, which have relatively good low temperature fixability, can be used as the binder resin, but have the following disadvantage. Specifically, in the methods, a high molecular weight material is added in a process, in which toner constituents such as binder resins and colorants are dissolved or dispersed in a solvent, to improve the releasability of the resultant toner, i.e., to impart a good oil-less fixing property to the resultant toner. Therefore, a manufacturing problem in that the viscosity of the toner composition liquid in which a solution or dispersion including toner constituents is dispersed increases occurs. This problem has not yet been solved.

[0012] JP-A 09-15903 discloses a toner prepared by a solution suspension method, which has spherical form and whose surface is roughened to have asperities. It is described therein that good cleanability can be imparted to the toner. However, the asperities of the surface of the toner do not have regularity, and therefore the toner has poor charge stability. In addition, controlling and optimization of molecular weight of the binder resin of the toner are not performed, and therefore a good combination of durability and releasability cannot be imparted to the toner.

[0013] Because of these reasons, a need exists for a toner which has relatively small particle diameter and sharp particle diameter distribution so as to produce high quality images with good fine dot reproducibility while having a good combination of cleanability and low temperature fixability and which hardly causes the toner adhesion problem (i.e., hardly deteriorates the chargeability of the carrier used even after long repeated use.

SUMMARY OF THE INVENTION

[0014] As an aspect of the present invention, a toner is provided which includes at least a binder resin, a colorant, a release agent and an inorganic filler, wherein the release agent includes a paraffin wax having a melting point of from 60˚C to 90 ˚C, and the inorganic filler includes montmorillonite or modified montmorillonite. In addition, the toner has a circularity of not less than 0.94 and a thermal property such that when the toner is subjected to a differential scanning calorimetric (DSC) analysis, the endothermic quantity calculated from the endothermic peak specific to the paraffin wax is from 3.0 J/g to 6.0 J/g. Further, the toner has a fluidity such that when a cone-shaped rotor having an apex angle of 60 degree and rotated at a speed of 1 rpm is entered into a toner layer by 20 mm in depth at an entering speed of 5 mm /sec, the torque generated by the toner is from 1.4 mNm to 2.0 mNm. In this regard, the toner layer is prepared by feeding the toner in a cylinder with a diameter of 60 mm and pressing the toner for 60 seconds under a load of 585 g (i.e., at a pressure of 2028.6 Pa (20.7gf/cm^2)).

[0015] As another aspect of the present invention, a process cartridge is provided which includes at least an image bearing member configured to bear an electrostatic image, and a developing device configured to develop the electrostatic image with a developer including the toner mentioned above to form a toner image on the image bearing member, wherein the process cartridge is detachably attached to an image forming apparatus as a unit. The process cartridge can include one or more other devices such as charging device configured to charge the image bearing member, light irradiating devices configured to irradiate the charged image bearing member with light to form an electrostatic image on the image bearing member, transfer devices configured to transfer a toner image on the image bearing member to an intermediate transfer medium or a receiving material, and cleaning devices configured to remove particles of the toner remaining on the image bearing member even after the toner image is transferred.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] Various other objects, features and attendant advantages of the present invention will be more fully appreciated

as the same becomes better understood from the detailed description when considered in connection with the accompanying drawing (s) in which like reference characters designate like corresponding parts throughout and wherein:

FIG. 1 is a schematic view illustrating an instrument for measuring the fluidity of toner using a cone-shaped rotor;
FIGS. 2A and 2B are schematic views illustrating the cone-shaped rotor of the instrument illustrated in FIG. 1;
FIGS. 3A, 3B and 3C are schematic views illustrating other cone-shaped rotors for use in the instrument illustrated in FIG. 1;
FIG. 4 is a schematic view illustrating another instrument for measuring the fluidity of toner using a cone-shaped rotor;
FIG. 5 is a schematic view for explaining the shape factor SF-1;
FIG. 6 is a schematic view for explaining the shape factor SF-2;
FIG. 7 is a schematic view illustrating the original image used for evaluating the cleanability of toner; and
FIG. 8 is a schematic view illustrating an example of the process cartridge of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0017] The toner of the present invention includes at least a binder resin, a colorant, a release agent and an inorganic filler. The toner constituents will be explained in detail.

Binder resin

[0018] Known resins can be used for the binder resin of the toner of the present invention. Specific examples of the resins include styrene resins, vinyl chloride resins, rosin-modified maleic acid resins, phenolic resins, epoxy resins, saturated polyester resins, unsaturated polyester resins, (low molecular weight) polyethylene resins, (low molecular weight) polypropylene resins, ionomer resins, polyurethane resins, silicone resins, ketone resins, ethylene - ethyl acrylate copolymers, xylene resins, polyvinylbutyral resins, etc. These resins can be used alone or in combination. It is preferable that the binder resin includes a resin, which is obtained in an aqueous medium by a crosslinking reaction or a polymer chain growth reaction. The details of such a resin will be described later.

[0019] The glass transition temperature (Tg) of the binder resin is generally from 40 to 70 ˚C, and preferably from 40 to 60 ˚C. When the glass transition temperature is too low, the high temperature preservability deteriorates. In contrast, when the glass transition temperature is too high, the low temperature fixability deteriorates. When the binder resin includes a modified polyester resinsuch asurea-modified polyester resins, the resultant toner has better high temperature preservability than conventional toners even when the glass transition temperature of the binder resin is lower than those of the polyester resins used as the binder resins of the conventional toners.

[0020] The binder component will be explained in detail.

(Modified polyester resin)

[0021] The toner of the present invention preferably includes a modified polyester resin (i) as a binder resin. The modified polyester resin is defined as a polyester resin which has a group other than ester groups or a polyester resin which includes a resin unit which has a covalent bond or an ionic bond with the polyester resin. Specifically, the modified polyester resin is defined as a polyester resin, which is prepared by incorporating a functional group (such as isocyanate groups), which can be reacted with a group having an active hydrogen atom (such as carboxylic acid groups and hydroxyl groups), in an end portion of a polyester resin, and then reacting the polyester resin having such a functional group with a compound having an active hydrogen atom (such as amines) to modify the end portion of the polyester resin, resulting in preparation of a modified polyester resin.

[0022] Suitable resins for use as the modified polyester resin (i) include urea-modified polyester resins, which are prepared by reacting a polyester prepolymer (A) having an isocyanate group with an amine (B). Specific examples of the polyester prepolymers (A) include prepolymers, which are prepared by reacting a polyester resin including a group having an active hydrogen, which is prepared by subjecting a polyhydric alcohol (PO) and a polycarboxylic acid (PC) to a polycondensation reaction, with a polyisocyanate compound (PIC). Specific examples of the group having an active hydrogen include hydroxyl groups (such as alcoholic hydroxyl groups and phenolic hydroxyl groups), amino groups, carboxyl groups, mercapto groups, etc. Among these groups, alcoholic hydroxyl groups are preferable.

[0023] Diols (DIO) and polyols (TO) having 3 or more hydroxyl groups can be used as the polyhydric alcohol (PO).

[0024] Specific examples of the diols (DIO) include alkylene glycol (e.g., ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 1,4-butanediol and 1,6-hexanediol); alkylene ether glycols (e.g., diethylene glycol, triethylene glycol, dipropylene glycol, polyethylene glycol, polypropylene glycol and polytetramethylene ether glycol); alicyclic diols (e.g., 1,4-cyclohexane dimethanol and hydrogenated bisphenol A); bisphenols (e.g., bisphenol A, bisphenol F, bisphenol S, 4,4'-dihydroxybiphenyls (e.g., 3,3'-difluoro-4,4'-dihydroxybiphenyl), bis(hydroxyphenyl)alkanes (e.g., bis(3-fluoro-4-hy-

droxyphenyl)methane, 1-phenyl-1,1-bis(3-fluoro-4-hydroxyphenyl)ethane, 2,2-bis(3-fluoro-4-hydroxyphenyl)propane, 2,2-bis(3,5-difluoro-4-hydroxyphenyl)propane (i.e., tetrafluorobisphenol A), and 2,2-bis(3-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane, and bis(4-hydroxyphenyl)ethers (e.g., bis(3-fluoro-4-hydroxyphenyl)ether));adductsofthe alicyclic diols mentioned above with an alkylene oxide (e.g., ethylene oxide, propylene oxide and butylene oxide); adducts of the bisphenols mentioned above with an alkylene oxide (e.g., ethylene oxide, propylene oxide and butylene oxide); etc.

[0025] Among these compounds, alkylene glycols having from 2 to 12 carbon atoms and adducts of bisphenols with an alkylene oxide are preferable. More preferably, alkylene oxide adducts of bisphenols, and mixtures of an alkylene oxide adduct of bisphenols with an alkylene glycol having from 2 to 12 carbon atoms are used.

[0026] Specific examples of the polyols (TO) include aliphatic alcohols having three or more hydroxyl groups (e.g., glycerin, trimethylol ethane, trimethylol propane, pentaerythritol and sorbitol); polyphenols having three or more hydroxyl groups (trisphenol PA, phenol novolak and cresol novolak); alkylene oxide adducts of the polyphenols mentioned above; etc.

[0027] These diols and polyols can be used alone or in combination.

[0028] It is preferable to use one or more diols (DIO) or a combination of a diol (DIO) with a small amount of polyol (TO) as the polyhydric alcohol (PO).

[0029] Dicaroxylic acids (DIC) and polycarboxylic acids (TC) having 3 or more carboxyl groups can be used as the polycarboxylic acid (PC).

[0030] Specific examples of the dicarboxylic acids (DIC) include alkylene dicarboxylic acids (e.g., succinic acid, adipic acid and sebacic acid); alkenylene dicarboxylic acids (e.g., maleic acid and fumaric acid); aromatic dicarboxylic acids (e.g., phthalic acid, isophthalic acid, terephthalic acid, and naphthalene dicarboxylic acids; etc.

[0031] Among these compounds, alkenylene dicarboxylic acids having 4 to 20 carbon atoms and aromatic dicarboxylic acids having 8 to 20 carbon atoms are preferably used as the dicarboxylic acid (DIC).

[0032] Specific examples of the polycarboxylic acids (TC) having three or more hydroxyl groups include aromatic polycarboxylic acids having from 9 to 20 carbon atoms (e.g., trimellitic acid and pyromellitic acid).

[0033] As for the polycarboxylic acid (PC), anhydrides or lower alkyl esters (e.g., methyl esters, ethyl esters or isopropyl esters) of the polycarboxylic acids mentioned above can be used for the reaction with a polyhydric alcohol (PO).

[0034] These dicarboxylic acids and polycarboxylic acids can be used alone or in combination.

[0035] It is preferable to use one or more dicarboxylic acids (DIC) or a combination of a dicarboxylic acid (DIC) with a small amount of polycarboxylic acid (TC) as the polycarboxylic acid (PC).

[0036] Suitable mixing ratio (i.e., an equivalence ratio [OH]/[COOH]) of a polyol (PO) to a polycarboxylic acid (PC) is from 2/1 to 1/1, preferably from 1.5/1 to 1/1 and more preferably from 1.3/1 to 1.02/1.

[0037] Specific examples of the polyisocyanates (PIC) for use in preparing modified polyester resins include aliphatic polyisocyanates (e.g., tetramethylene diisocyanate, hexamethylene diisocyanate and 2,6-diisocyanate methylcaproate); alicyclic polyisocyanates (e.g., isophorone diisocyanate and cyclohexylmethane diisocyanate); aromatic diisocianates (e.g., tolylene diisocyanate and diphenylmethane diisocyanate); aromatic aliphatic diisocyanates (e.g., α, α, α', α'-tetramethyl xylylene diisocyanate); isocyanurates; blocked polyisocyanates in which the polyisocyanates mentioned above are blocked with phenol derivatives, oximes or caprolactams; etc. These compounds can be used alone or in combination.

[0038] Suitable mixing ratio (i.e., the equivalence ratio [NCO]/[OH]) of the [NCO] group of a polyisocyanate (PIC) to the [OH] group of a polyester is from 5/1 to 1/1, preferably from 4/1 to 1.2/1 and more preferably from 2.5/1 to 1.5/1. When the [NCO]/[OH] ratio is too large, the low temperature fixability of the toner deteriorates. In contrast, when the ratio is too small, the content of the urea group in the modified polyesters decreases, thereby deteriorating the hot-offset resistance of the toner.

[0039] The content of the polyisocyanate unit in the polyester prepolymer (A) having an isocyanate group is from 0.5 to 40 % by weight, preferably from 1 to 30 % by weight, and more preferably from 2 to 20 % by weight. When the content is too low, the hot offset resistance of the toner deteriorates and in addition a good combination of preservability and low temperature fixability cannot be imparted to the resultant toner. In contrast, when the content is too high, the low temperature fixability of the toner deteriorates.

[0040] The average number of the isocyanate group included in a molecule of the polyester prepolymer (A) is generally not less than 1, preferably from 1.5 to 3, and more preferably from 1.8 to 2.5. When the average number of the isocyanate group is too small, the molecular weight of the resultant urea-modified polyester (which is crosslinked and/or extended) decreases, thereby deteriorating the hot offset resistance of the resultant toner.

[0041] The urea-modified polyester resin for use as a binder resin of the toner of the present invention can be prepared by reacting a polyester prepolymer (A) having an isocyanate group with an amine (B).

[0042] Specific examples of the amines (B) include diamines (B1), polyamines (B2) having three or more amino groups, amino alcohols (B3), amino mercaptans (B4), amino acids (B5) and blocked amines (B6) in which the amines (B1-B5) mentioned above are blocked. These amines can be used alone or in combination.

[0043] Specific examples of the diamines (B1) include aromatic diamines (e.g., phenylene diamine, diethyltoluene

diamine and 4,4'-diaminodiphenyl methane); alicyclic diamines (e.g., 4,4'-diamino-3,3'-dimethyldicyclohexyl methane, diaminocyclohexane and isophoron diamine); aliphatic diamines (e.g., ethylene diamine, tetramethylene diamine and hexamethylene diamine); etc.

[0044] Specific examples of the polyamines (B2) having three or more amino groups include diethylene triamine, triethylene tetramine, etc. Specific examples of the amino alcohols (B3) include ethanol amine, hydroxyethyl aniline, etc. Specific examples of the amino mercaptan (B4) include aminoethyl mercaptan, aminopropyl mercaptan, etc. Specific examples of the amino acids (B5) include aminopropionic acid, aminocaproic acid, etc. Specific examples of the blocked amines (B6) include ketimine compounds which are prepared by reacting one of the amines (B1-B5) mentioned above with a ketone such as acetone, methyl ethyl ketone and methyl isobutyl ketone; oxazoline compounds, etc. Among these amines, diamines (B1) and mixtures of a diamine (B1) with a small amount of polyamine (B2) are preferably used.

[0045] The molecular weight of the urea-modified polyesters can be controlled using a polymer chain growth inhibitor. Specific examples of the polymer chain growth inhibitor include monoamines (e.g., diethyl amine, dibutyl amine, butyl amine and lauryl amine), and blocked amines (i.e., ketimine compounds) prepared by blocking the monoamines mentioned above.

[0046] The mixing ratio (i.e., the equivalence ratio [NCO] / [NHx]) of the [NCO] group of the prepolymer (A) having an isocyanate group to the [NHx] group of the amine (B) is from 1/2 to 2/1, preferably from 1/1.5 to 1.5/1 and more preferably from 1/1.2 to 1.2/1. When the mixing ratio is too low or too high, the molecular weight of the resultant urea-modified polyester decreases, resulting in deterioration of the hot offset resistance of the resultant toner.

[0047] The toner of the present invention preferably includes a urea-modified polyester resin (UMPE) as a binder resin. In this regard, the urea-modified polyester resin can include a urethane bonding as well as a urea bonding. The molar ratio of the urea bonding to the urethane bonding is from 100/0 to 10/90, preferably from 80/20 to 20/80, and more preferably from 60/40 to 30/70. When the molar ratio of the urea bonding is too low, the hot offset resistance of the resultant toner deteriorates.

[0048] The modified polyesters (i) such as urea-modified polyester resins can be prepared, for example, by a method such as one-shot methods or prepolymer methods. The weight average molecular weight of the modified polyesters is generally not less than 10,000, preferably from 20,000 to 10,000,000 and more preferably from 30,000 to 1,000,000. When the weight average molecular weight is too low, the hot offset resistance of the resultant toner deteriorates. In contrast, when the weight average molecular weight is too high, the problems which occur are that the fixability of the resultant toner deteriorates, and it becomes difficult to prepare toner particles when the toner is prepared by a granulation method or to pulverize the kneaded mixture of toner constituents when the toner is prepared by a pulverization/classification method.

[0049] The number average molecular weight of the modified polyester resin (i) is not particularly limited if an unmodified polyester resin is used in combination there with. Specifically, the weight average molecular weight of the modified polyester resin (i) is mainly controlled rather than the number average molecular weight. When the modified polyester resin (i) is used alone, the number average molecular weight of the resin is preferably not greater than 20,000, preferably from 1,000 to 10, 000, and more preferably from 2, 000 to 8, 000. When the number average molecular weight is too high, the low temperature fixability of the resultant toner deteriorates. In addition, when the resultant toner is used as a color toner used for full color image forming apparatus, the toner has low glossiness.

[0050] The molecular weight of the modified polyesters (i) can be controlled using a molecular chain growth inhibitor. Specific examples of the molecular chain growth inhibitor include monoamines (e.g., diethyl amine, dibutyl amine, butyl amine and lauryl amine), and blocked amines (i.e., ketimine compounds) prepared by blocking the monoamines mentioned above.

(Unmodified polyester resin)

[0051] It is preferable for the toner of the present invention to include a combination of a modified polyester resin (i) (such as urea-modified polyester resins) with an unmodified polyester resin (ii) as the binder resin thereof. By using such a combination, the low temperature fixability of the toner can be improved and in addition the toner can produce color images having a high glossiness.

[0052] Suitable materials for use as the unmodified polyester resin (ii) include polycondensation products of a polyol (PO) with a polycarboxylic acid (PC). Specific examples of the polyol (PO) and polycarboxylic acid (PC) are mentioned above for use in preparing the modified polyester resin (i). In addition, specific examples of the suitable polyol and polycarboxylic acid are also mentioned above.

[0053] In this regard, polyester resins including a bond (such as urethane bond) other than a urea bond are considered as the unmodified polyester resin (II) in the present application.

[0054] When a combination of a modified polyester resin with an unmodified polyester resin is used as the binder resin, it is preferable that the modified polyester resin is at least partially mixed with the unmodified polyester resin to improve the low temperature fixability and hot offset resistance of the toner. Namely, it is preferable that the modified

polyester resin has a molecular structure similar to that of the unmodified polyesterresin. Themixingratio (i/ii) ofamodifiedpolyester resin (i) to an unmodified polyester resin (ii) is from 5/95 to 80/20, preferably from 5/95 to 30/70, more preferably from 5/95 to 25/75, and even more preferably from 7/93 to 20/80. When the added amount of the modified polyester resin (i) is too small, the hot offset resistance of the toner deteriorates and in addition, it is impossible to impart a good combination of high temperature preservability and low temperature fixability to the toner.

[0055] The molecular weight (peak molecular weight) of the unmodifiedpolyester resin (ii) is generally from 1, 000 to 10, 000, preferably from 2, 000 to 8, 000, and more preferably from 2, 000 to 5,000. When the molecular weight is too low, the high temperature preservability of the toner deteriorates. In contrast, when the molecular weight is too high, the low temperature fixability of the toner deteriorates.

[0056] The hydroxyl value of the unmodified polyester resin (ii) is preferably not less than 5 mgKOH/g, more preferably from 10 to 120 mgKOH/g, and even more preferably from 20 to 80 mgKOH/g. When the hydroxyl value is too low, a good combination of high temperature preservability and low temperature fixability cannot be imparted to the toner.

[0057] The acid value of the unmodified polyester resin (ii) is preferably from 1 to 5 mgKOH/g, and more preferably from 2 to 4 mgKOH/g.

[0058] The glass transition temperature (Tg) of the binder resin is generally from 35 to 70 ˚C, and preferably from 55 to 65 ˚C. When the glass transition temperature is too low, the high temperature preservability of the toner deteriorates. In contrast, when the glass transition temperature is too high, the low temperature fixability of the toner deteriorates.

[0059] When a urea-modified polyester resin is used as a binder resin, the urea-modified polyester resin tends to be present in a surface portion of the toner particles. Therefore, the resultant toner has better high temperature preservability than conventional toners including one or more conventional polyester resins as the binder resin even when the toner has a lower glass transition temperature than the conventional toners.

Colorants

[0060] The toner of the present invention includes a colorant. Suitable materials for use as the colorant include known dyes and pigments.

[0061] Specific examples of the dyes and pigments include carbon black, Nigrosine dyes, black iron oxide, NAPHTHOL YELLOW S, HANSA YELLOW 10G, HANSA YELLOW 5G, HANSA YELLOW G, Cadmium Yellow, yellow iron oxide, loess, chrome yellow, Titan Yellow, polyazo yellow, Oil Yellow, HANSA YELLOW GR, HANSA YELLOW A, HANSA YELLOW RN, HANSA YELLOW R, PIGMENT YELLOW L, BENZIDINE YELLOW G, BENZIDINE YELLOW GR, PERMANENT YELLOW NCG, VULCAN FAST YELLOW 5G, VULCAN FAST YELLOW R, Tartrazine Lake, Quinoline Yellow LAKE, ANTHRAZANE YELLOW BGL, isoindolinone yellow, red iron oxide, red lead, orange lead, cadmium red, cadmium mercury red, antimony orange, Permanent Red 4R, Para Red, Fire Red, p-chloro-o-nitroaniline red, Lithol Fast Scarlet G, Brilliant Fast Scarlet, Brilliant Carmine BS, PERMANENT RED F2R, PERMANENT RED F4R, PERMANENT RED FRL, PERMANENT RED FRLL, PERMANENT RED F4RH, Fast Scarlet VD, VULCAN FAST RUBINE B, Brilliant Scarlet G, LITHOL RUBINE GX, Permanent Red F5R, Brilliant Carmine 6B, Pigment Scarlet 3B, Bordeaux 5B, Toluidine Maroon, PERMANENT BORDEAUX F2K, HELIO BORDEAUX BL, Bordeaux 10B, BON MAROON LIGHT, BON MAROON MEDIUM, Eosin Lake, Rhodamine Lake B, Rhodamine Lake Y, Alizarine Lake, Thioindigo Red B, Thioindigo Maroon, Oil Red, Quinacridone Red, Pyrazolone Red, polyazo red, Chrome Vermilion, Benzidine Orange, perynone orange, Oil Orange, cobalt blue, cerulean blue, Alkali Blue Lake, Peacock Blue Lake, Victoria Blue Lake, metal-free Phthalocyanine Blue, Phthalocyanine Blue, Fast Sky Blue, INDANTHRENE BLUE RS, INDANTHRENE BLUE BC, Indigo, ultramarine, Prussian blue, Anthraquinone Blue, Fast Violet B, Methyl Violet Lake, cobalt violet, manganese violet, dioxane violet, Anthraquinone Violet, Chrome Green, zinc green, chromium oxide, viridian, emerald green, Pigment Green B, Naphthol Green B, Green Gold, Acid Green Lake, Malachite Green Lake, Phthalocyanine Green, Anthraquinone Green,titaniumoxide,zinc oxide, lithopone and the like. These materials are used alone or in combination.

[0062] The content of the colorant in the toner is preferably from 1% to 15 % by weight, and more preferably from 3% to 10 % by weight based on the weight of the toner.

[0063] Master batches, which are complexes of a colorant with a resin (binder resin) , can be used as the colorant of the toner of the present invention.

[0064] Specific examples of the resins for use as the binder resin of the master batches include styrene polymers and substituted styrene polymers such as polystyrene, poly-p-chlorostyrene and polyvinyl toluene; copolymers of styrene (or substituted styrene) and vinyl compounds; and other resins such as polymethyl methacrylate, polybutyl methacrylate, polyvinyl chloride, polyvinyl acetate, polyethylene, polypropylene, polyesters, epoxy resins, epoxy polyol resins, polyurethane resins, polyamide resins, polyvinyl butyral resins, acrylic resins, rosin, modified rosins, terpene resins, aliphatic or alicyclic hydrocarbon resins, aromatic petroleum resins, chlorinated paraffin, paraffin waxes, etc. These resins are used alone or in combination.

[0065] The master batches can be prepared by mixing one or more of the resins as mentioned above and one or more of the colorants as mentioned above, and kneading the mixture while applying a high shearing force thereto. In

this case, an organic solvent can be added to increase the interaction between the colorant and the resin. In addition, a flushing method in which an aqueous paste including a colorant and water is mixed with a resin dissolved in an organic solvent, the mixture is kneaded to transfer the colorant to the resin side (i.e., the oil phase), and then the organic solvent (and water, if desired) is removed from the kneaded mixture can be preferably used because the resultant wet cake can be used without being dried. When performing the mixing and kneading process, dispersing devices capable of applying a high shearing force such as three roll mills can be preferably used.

Release agent

[0066] The toner of the present invention includes a release agent. Specific examples of the release agent include waxes. Among the waxes, paraffin waxes having a melting point of from 60 to 90 ˚C are preferably used. When such a paraffin wax is included in the toner, the wax is dispersed in the binder resin. When a toner image constituted of the toner is fixed, the wax dispersed in the binder resin is present between the fixing roller and the toner, and functions as a release agent in the fixing process. Therefore, even when a release agent is not applied to the fixing roller, the toner image can be well fixed without causing a hot offset problem in that part of a toner image is adhered to a fixing member and the part of toner image is re-transferred to a receiving material, resulting in formation of a defective image.

[0067] In this application, the melting point of a paraffin wax is determined as the temperature at which the maximum endothermic peak is observed when the wax is subjected to a differential scanning calorimetry (DSC) analysis.

[0068] In addition, it is preferable that when the toner is subjected to a DSC analysis, the endothermic quantity calculated from the endothermic peak specific to the release agent is from 3.0 to 6.0 J/g.

[0069] When the added amount of a paraffin wax is too small, the toner has poor releasability.

Inorganic filler

[0070] The toner of the present invention includes an inorganic filler. Specific examples of such an inorganic filler include silica, alumina, titania, montmorillonite, modified montmorillonite (such as CLAYTON APA from Southern Clay Products Co., Ltd.), in which one or more organic ions are incorporated asinterlayerions,etc. Among these materials, montmorillonite and modified montmorillonite are preferably used.

[0071] Suitable organic compounds for use in incorporating organic ions in montmorillonite include quaternary alkyl ammonium salts, phosphonium salts, imidazolium salts, etc. Among these compounds, quaternary alkyl ammonium salts are preferable. Specific examples of the quaternary alkyl ammonium salts include trimethylstearyl ammonium, dimethylstearylbenzyl ammonium, dimethyloctadecyl ammonium, oleylbis(2-hydroxyethyl)methyl ammonium, etc.

[0072] Specific examples of other organic compounds for use in incorporating organic ions montmorillonite include sulfates, sulphonates, carboxylates,and phosphates having a group (or a structure) such as linear, branched or cyclic alkyl groups (C1-C44), alkenyl groups (C1-C22), alkoxyl groups (C8-C32), hydroxyalkyl groups (C2-C22), ethylene oxide structures, and propylene oxide structures. Among these compounds, carboxylic acids having an ethylene oxide structure are preferably used.

[0073] By including such an inorganic filler in the toner, the surface of the toner particles is roughened. The mechanism of roughening the surface of the toner particles is as follows. Specifically, in a toner preparation method in which a toner composition liquid prepared by dissolving or dispersing toner constituents including at least a binder resin, a colorant, a release agent (such as paraffin waxes) and an inorganic filler (such as montmorillonite and modified montmorillonite) in a solvent is emulsified in an aqueous medium in the presence of a surfactant and/or a particulate resin, the inorganic filler moves toward the interface between droplets of the toner composition liquid and the aqueous medium in which the droplets are dispersed. When the solvent in the droplets is removed after an optional reaction (such as crosslinking reactions and polymer chain growth reactions of a binder resin precursor), the inorganic filler remains in the surface portion thereof, resulting in formation of toner particles having a rough surface.

[0074] In order to prepare toner particles having such a rough surface, the added amount of the inorganic filler is preferably from 0.1 to 10 parts by weight, per 100 parts by weight of the binder resin included in the toner. In this regard, the more the added amount of an inorganic filler, the greater the shape factors (SF-1 and SF-2 mentioned later) of the resultant toner, i.e., the more roughed surface (i.e., the more deformed particle form) the resultant toner has.

Charge controlling agent

[0075] The toner of the present invention optionally includes a charge controlling agent. Known charge controlling agents for use in conventional toners can be used for the toner of the present invention.

[0076] Specific examples of the charge controlling agents include Nigrosine dyes, triphenyl methane dyes, chromium-containing metal complex dyes, molybdic acid chelate pigments, Rhodamine dyes, alkoxyamines, quaternary ammonium salts, fluorine-modified quaternary ammonium salts, alkylamides, phosphor and its compounds, tungsten and its com-

pounds, fluorine-containing activators, metal salts of salicylic acid, metal salts of salicylicacidderivatives, etc. These materials can be used alone or in combination.

[0077] Specific examples of the marketed charge controlling agents include BONTRON 03 (Nigrosine dye), BONTRON P-51 (quaternary ammonium salt), BONTRON S-34 (metal-containing azo dye), BONTRON E-82 (metal complex of oxynaphthoic acid), BONTRON E-84 (metal complex of salicylic acid), and BONTRON E-89 (phenolic condensation product), which are manufactured by Orient Chemical Industries Co., Ltd.; TP-302 and TP-415 (molybdenum complex of quaternary ammonium salt), which are manufactured by Hodogaya Chemical Co., Ltd.; COPY CHARGE PSY VP2038 (quaternary ammonium salt), COPY BLUE (triphenyl methane derivative), COPY CHARGE NEG VP2036 and COPY CHARGE NX VP434 (quaternary ammonium salt), which are manufactured by Hoechst AG; LRA-901, and LR-147 (boron complex), which are manufactured by Japan Carlit Co., Ltd.; copper phthalocyanine, perylene, quinacridone, azo pigments, and polymers having a functional group such as a sulfonate group, a carboxyl group, a quaternary ammonium group, etc.

[0078] The content of the charge controlling agent in the toner of the present invention is determined depending on the variables such as choice of binder resin, presence of additives, and dispersion method. In general, the content of the charge controlling agent is preferably from 0.1 parts to 10 parts by weight, and more preferably from 0.2 parts to 5 parts by weight, per 100 parts by weight of the binder resin included in the toner. When the content is too high, the charge quantity of the toner excessively increases, and thereby the electrostatic attraction between the developing roller and the toner increases, resulting in deterioration of fluidity and decrease of image density.

External additive

[0079] The toner of the present invention preferably includes an external additive.

[0080] Inorganic fine particles are typicallyused as the external additive. Inorganic particulate materials having a primary particle diameter of from 5 nm to 2 μm, and preferably from 5 nm to 500 nm, are used. The surface area of the inorganic particulate materials is preferably from 100 m^2/g to 500 m^2/g when measured by a BET method.

[0081] The content of an inorganic particulate material in the toner is preferably from 0.01% to 5.0% by weight, and more preferably from 0.01% to 2.0% by weight, based on the total weight of the toner.

[0082] Specific examples of such inorganic particulate materials include silica, alumina, titanium oxide, barium titanate, magnesium titanate, calcium titanate, strontium titanate, zinc oxide, tin oxide, quartz sand, clay, mica, sand-lime, diatom earth, chromium oxide, cerium oxide, red iron oxide, antimony trioxide, magnesium oxide, zirconium oxide, barium sulfate, barium carbonate, calcium carbonate, silicon carbide, silicon nitride, etc.

[0083] In addition, particulate polymers can also be used as the external additive. Specific examples of the particulate polymers include particles of polymers and copolymers of styrene, and methacrylates and acrylates, which are prepared by a method such as soap-free emulsion polymerization methods, suspension polymerization methods, and dispersion polymerization methods; polycondensation resins such as silicone resins, benzoguanamine resins and nylon resins; and thermosetting resins.

[0084] The external additive used for the toner is preferably subjected to a hydrophobizing treatment to prevent deterioration of the fluidity and charge properties of the resultant toner particularly under high humidity conditions. Suitable hydrophobizing agents for use in the hydrophobizing treatment include silane coupling agents, silylating agents, silane coupling agents having a fluorinated alkyl group, organic titanate coupling agents, aluminum coupling agents, silicone oils,modifiedsilicone oils, etc. Particularly, hydrophobized silica and hydrophobized titanium oxide are preferably used as the external additive.

Method for preparing toner

[0085] The toner of the present invention can be prepared by a pulverization/classification method which includes the steps of kneading toner constituents including at least a binder resin, a colorant, a release agent and an inorganic filler while heating; cooling the kneaded toner constituents; pulverizing the cooled toner constituents; classifying the pulverized toner constituents to prepare toner particles; and then mixing an external additive with the toner particles to prepare the toner. However, it is preferable to use a wet granulation method which includes the steps of dissolving or dispersing toner constituents including at least a polyester prepolymer having a functional group including a nitrogen atom, a polyester resin, a colorant, a release agent and an inorganic filler in an organic solvent to prepare a toner composition liquid; and then subjecting the toner composition liquid (the prepolymer) to a crosslinking reaction and/or a polymer chain growth reaction in an aqueous medium to prepare toner particles in the aqueous medium.

[0086] The wet granulation method will be explained in detail.

[0087] Specifically, the method is such that toner constituents including at least a binder component, which includes at least a polyester prepolymer reactive with an active hydrogen atom (i.e., a precursor of a binder resin), a colorant, a wax and an inorganic filler are dissolved or dispersed in an organic solvent to prepare a toner composition liquid; reacting

the toner composition liquid (i.e., the prepolymer) with a crosslinking agent and/or a polymer chain growing agent in an aqueous medium including a dispersant such that the polyester prepolymer is changed to a binder resin (such as modified polyester resins); and removing the solvent from the dispersion (emulsion) to prepare a dispersion of toner particles.

[0088] Next, the properties of the toner of the present invention will be explained.

[0089] The toner of the present invention has a circularity of not less than 0.94.

[0090] The circularity of a particle is determined by the following equation:

$$\text{Circularity} = L1/L2,$$

wherein L2 represents the length of the circumference of the projected image of a particle and L1 represents the length of the circumference of a circle having the same area as that of the projected image of the particle. The average circularity can be determined by averaging the circularities of a number of toner particles.

[0091] In this application, the circularity of toner is measured with a flow-type particle image analyzer FPIA-2100 from Sysmex Corp. The procedure of the measurement is as follows.

(1) at first 100 ml of water from which solid foreign materials have been removed, 0.5 ml of a surfactant (NEOGEN SC-A from Daiichi Kogyo Seiyaku Co., Ltd.), which serves as a dispersant and 0.5 g of a sample (i.e., toner) are mixed;
(2) the mixture is subjected to a supersonic dispersion treatment for about 3 minutes using a supersonic dispersion machine to prepare a dispersion including particles of the sample at a concentration of from 3,000 to 10,000 pieces/μl;
(3) the dispersion is passed through a detection area formed on a plate in the instrument; and
(4) the particles are optically detected by a CCD camera and then the shapes thereof are analyzed with an image analyzer, resulting in determination of the average circularity of the sample (toner).

[0092] In addition, the toner has a fluidity such that when a cone-shaped rotor having an apex angle of 60 degree and rotated at a speed of 1 rpm is entered into a toner layer by 20 mm in depth at an entering speed of 5 mm /sec, which toner layer is prepared by feeding the toner in a cylinder with a diameter of 60 mm and pressing the toner for 60 seconds under a load of 585 g (i.e., at a pressure of 2028.6 Pa (20.7 gf/cm^2), the torque generated by the toner is from 1.4 mNm to 2.0 mNm.

[0093] When the torque is too low or too high, the toner tends to be adhered to the surface of carrier particles, which are mixed to prepare a two component developer, resulting in deterioration of the chargeability of the carrier particles. This problem is first discovered by the present inventors, and the mechanism thereof is considered as follows.

[0094] Specifically, a two component developer including a toner and a carrier is agitated in a developing device to charge the toner. In this regard, when the toner has a smooth surface, the area of the contact area between the surface of the toner and the carrier is small in the case of two component developer, and the area of the contact area between the surface of the toner and the developing sleeve serving as a developer bearing member is small in the case of one component developer. In these cases, the toner and the carrier or the developing sleeve make a point contact. Therefore, the toner particles tend to roll on the surface of the carrier or the developing sleeve, resulting in fixedly adhesion of the toner constitutional materials having a low melting point (such as waxes and resins), thereby deteriorating the charge-abilityof the carrier and the developing sleeve.

[0095] The present inventors discover that the smoothness of the surface of the toner can be determined by measuring the torque of the toner as mentioned above. It is discovered that when the torque is less than 1.2 mNm, this problem tends to be seriously caused.

[0096] In addition, when a toner has a rough surface and the torque of the toner is too high, the toner and a carrier or a developing sleeve make a plane contact. In this case, the toner particles hardly roll on the surface of the carrier and developing sleeve. However, the area of the toner contacted with the surface of the carrier and developing sleeve increases, and thereby the toner constitutional materials having a low melting point (such as waxes and resins) tend to be fixedly adhered thereto, resulting in deterioration of the chargeability of the carrier and the developing sleeve. The present inventors discover that when the torque is greater than 2.0 mNm, this problem tends to be caused.

[0097] Therefore, the torque is preferably controlled to fall in a range of from 1.2 to 2.0 mNm, and more preferably from 1.4 to 2.0 mNm.

[0098] When the toner of the present invention is prepared by a granulation method in which toner particles are prepared in an aqueous medium by a crosslinking reaction and/or a molecular chain growth reaction, the toner preferably has a first shape factor SF-1 of from 130 to 160, and a second shape factor SF-2 of from 110 to 140. The first shape factor SF-1 represents the degree of the roundness of the particles of the toner, and the second shape factor SF-2 represents the degree of the roughness of the surface of the toner particles. The methods for determining the shape factors SF-1 and SF-2 will be mentioned later.

[0099] As mentioned above, toner having a small average particle diameter and a sharp particle diameter distribution tends to cause the above-mentioned cleaning problem. By controlling the shape of the particles of the toner so that the first and second shape factors fall in the above-mentioned ranges, occurrence of the cleaning problem can be prevented.

[0100] The reason why the shape factors should be controlled will be explained below.

[0101] At first, the relationship between the shape of particles of toner and transferability of the toner will be explained. In full color copiers, the amount of toner particles constituting a color image formed on an image bearing member (such as photoreceptors) is larger than that of toner particles constituting a black image. Therefore, it is difficult to improve the transfer efficiency by using conventional toners having irregular forms. Further, when a conventional toner having irregular forms is used, the toner tends to be fixedly adhered to the surfaces of the photoreceptor and intermediate transfer medium used (or a toner film is formed on the surfaces) due to high shearing force and friction therebetween, resulting in deterioration of transferability of toner images. Particularly, in full color image forming apparatus, four color toner images cannot be evenly transferred to an intermediate transfer medium, thereby producing full color images with poor evenness and color balance. Namely, high quality full color images cannot be produced.

[0102] In order to balance the blade cleanability with transfer efficiency of a toner, it is preferable for the toner to have a first shape factor SF-1 of from 130 to 160. Although the cleanability of toner changes depending on the material used for the blade and the angle at which the blade is contacted with the image bearing member, and the transferability of toner changes depending on the transfer conditions, the toner of the present invention can have a good combination of cleanability and transferability when the toner has a SF-1 of from 130 to 160. When the SF-1 is too small, the cleanability of the toner deteriorates. In contrast, when the SF-1 is too large, the transferability of the toner deteriorates. Specifically, when the shape factor SF-1 is too large, the toner has a deformed shape, and thereby movement of the toner in transfer processes (e.g., transfer of the toner from the surface of a photoreceptor to a receiving material, from the surface of a photoreceptor to an intermediate transfer medium, from a first intermediate transfer medium to a second intermediate transfer medium, etc.) cannot be smoothly performed. In addition, the toner particles having different shapes exhibit different behaviors, and therefore the toner has a low transfer efficiency. Further, the toner is unstably charged. Furthermore, the toner is easily pulverized in a developing device because of being brittle, thereby generating fine toner particles in the developing device, resulting in shortening of the life of the toner.

[0103] The toner of the present invention preferably has a first shape factor SF-1 of from 130 to 160 and a spindle form. Toner having a spindle form has a good transferability close to that of a spherical toner because the surface of the toner does not have large asperities. In addition, toner having a spindle form also has a good cleanability. Therefore, toner having a spindle form has a good combination of transferability and cleanability, although in general cleanability and transferability of toner tend to establish a trade-off relationship.

[0104] Toner prepared by a pulverization/classification method has irregular forms, i.e., does not have a certain particle form and roundness, and the shape factor of the toner is generally greater than 140. In addition, the toner has a broad particle diameter distribution. Therefore, it is difficult to control the ratio D4/Dn of the weight average particle diameter (D4) of the toner to the number average particle diameter (Dn) thereof to be not greater than 1.30.

[0105] When toner is prepared by a polymerization method such as suspension polymerization and emulsion polymerization, it is difficult to use a polyester resin as the binder resin of the toner, and therefore, it is hard to improve the low temperature fixability. The toners prepared by the methods disclosed in JP-As 11-149180 and 2000-292981, in which toner particles including a colorant and a binder resin are prepared in an aqueous medium by subjecting a prepolymer (i.e., a precursor of the binder resin) having an isocyanate group to a crosslinking reaction and/or a molecular chain growth reaction using an amine to prepare the binder resin in the aqueous medium. However, the toners do not have a good combination of transferability and cleanability because the shape of the toner particles is not controlled.

[0106] The toner of the present invention preferably has a weight average particle diameter (D4) of from 3 to 8 μm, and a ratio (D4/Dn) of the weight average particle diameter (D4) to the number average particle diameter (Dn) of from 1.00 to 1.30. In this case, the toner can produce high definition and high quality images. In addition, variation of the particle diameter distribution of the toner is little and therefore the toner can maintain good developability even when the toner is agitated for a long period of time in a developing device while a fresh toner is supplied thereto. When the ratio D4/Dn is too large, variation of the particle diameter of the toner particles increases, and therefore the toner particles exhibit different behavior in a developing process, resulting in formation of images with poor fine dot reproducibility, i.e., formation of low quality image. The ratio D4/Dn is more preferably from 1.00 to 1.20 to produce higher quality images.

[0107] The weight average particle diameter (D4) of the toner is preferably from 3 to 8 μm. In general, using a toner having a small average particle diameter is advantageous in order to produce high definition and high quality images. However, such a small-sized toner is inferior in transferability and cleanability. When a toner having a weight average particle diameter (D4) smaller than the above-mentioned range is used for a two component developer, the toner tends to cause a toner adhesion problem in that the toner is fixedly adhered to a carrier after long term agitation, resulting in deterioration of the charging ability of the carrier. When such a small-sized toner is used as a one component developer, problems in that the toner forms a film on a developing roller, and the toner is fixedly adhered to members such as blades configured to form a thin toner layer on a developing roller tend to be caused. In addition, these phenomena are

largely influenced by the content of fine toner particles in the toner. Specifically, when toner particles having a particle diameter of not greater than 2 μm are included in the toner in an amount of greater than 10% by number, the toner adhesion problem is seriously caused and in addition the charge stability of the toner seriously deteriorates. Therefore, the content of toner particles having a particle diameter of not greater than 2 μm in the toner is preferably not greater than 10% by number.

[0108] In contrast, when the weight average particle diameter of the toner is larger than the above-mentioned range, it is difficult to produce high definition and high quality images and in addition a problem in that the particle diameter distribution of the toner in a two-component developer largely changes when the toner is used while replenishing a fresh toner to the developer, resulting in variation of image qualities tends to occur. The same is true for the case where the toner has too high a ratio D4/Dn.

[0109] The toner of the present invention preferably has a glass transition temperature (Tg) of from 40 to 60 ˚C. In this case, the toner has a good combination of low temperature fixability, high temperature fixability and durability. When the glass transition temperature of the toner is too low, the high temperature preservability of the toner deteriorates. In contrast, when the glass transition temperature of the toner is too high, the low temperature fixability of the toner deteriorates. When the toner includes a combination of a urea-modified polyester resin and an unmodified polyester resin as binder resins, the toner has a better high temperature preservability than known polyester-type toners including a conventional polyester resin as a binder resin.

[0110] The toner of the present invention preferably includes particles having a particle diameter of not greater than 2 μm in an amount of not greater than 10% by number. In this case, the toner has a good cleanability, and thereby clear images can be produced.

[0111] The toner of the present invention preferably has a glass transition temperature (Tg) of from 40 ˚C to 60 ˚C. When the toner has too low a glass transition temperature, the high temperature preservability of the toner deteriorates. In contrast, when the toner has too high a glass transition temperature, the low temperature fixability of the toner deteriorates.

[0112] Next, the method for preparing the toner of the present invention will be explained. The toner preparation method is not limited thereto.

Method for preparing binder resin

[0113] The modified polyester resins for use as binder resins of the toner of the present invention are typically prepared by the following method, but the preparation method is not limited thereto.

[0114] At first, a polyol (PO) and a polycarboxylic acid (PC) are heated to a temperature ranging from 150 to 280 ˚C in the presence of an esterification catalyst such as tetrabutoxy titanate and dibutyl tin oxide to be reacted. In this reaction, generated water is removed under a reduced pressure, if necessary. Thus, a polyester resin having a hydroxyl group is prepared. The thus prepared polyester resin is reacted with a polyisocyanate (PIC) at a temperature ranging from 40 to 140 ˚C to prepare a polyester prepolymer (A) having an isocyanate group. The prepolymer (A) is reacted with an amine (B) at temperature ranging from 0 to 140 ˚C to prepare a urea-modified polyester resin (UMPE). When the materials PIC, A and B are reacted, one or more solvents may be used if desired. Specific examples of the solvents include solvents inactive with PICs such as aromatic solvents (e.g., toluene and xylene); ketones (e.g., acetone, methyl ethyl ketone and methyl isobutyl ketone); esters (e.g., ethyl acetate); amides (e.g., dimethylformamide and dimethylacetamide); and ethers (e.g., tetrahydrofuran).

[0115] It is preferable to use a combination of a modified polyester resin and an unmodified polyester resin as the binder resin of the toner of the present invention. Such unmodified polyester resins can be prepared by a method similar to the method mentioned above for use in preparing the polyester resin having a hydroxyl group. The thus prepared polyester resin is mixed with the above-prepared modified polyester resin to prepare a binder resin solution.

Method for preparing toner

(1) Preparation of toner composition liquid

[0116] A toner composition liquid (i.e., oil phase liquid) is prepared by dissolving or dispersing toner constituents (such as colorants, unmodified polyester resins, polyester prepolymers having an isocyanate group (i.e., precursors of binder resins), and release agents) in an organic solvent. The organic solvent used is preferably removed after or in the toner particle preparation process.

[0117] Suitable organic solvents for use in the toner composition liquid include volatile solvents having a boiling point lower than 150 ˚C (preferably lower than 100 ˚C) so as to be easily removed from the emulsion. Specific examples of such volatile solvents include toluene, xylene, benzene, carbon tetrachloride, methylene chloride, 1,2-dichloroethane, 1,1,2-trichloroethane, trichloroethylene, chloroform, monochlorobenzene, dichloroethylidene, methyl acetate, ethyl ac-

etate, methyl ethyl ketone, and methyl isobutyl ketone. These solvents can be used alone or in combination. Among these organic solvents, aromatic solvents such as toluene, xylene, and benzene, and halogenated hydrocarbons such as methylene chloride, 1,2-dichloroethane, chloroform and carbon tetrachloride are preferably used. Although the content of the organic solvent in the toner composition liquid is determined depending on the targeted properties of the resultant toner particles, the weight ratio of the organic solvent to the polyester prepolymer is generally from 0/100 to 300/100, preferably from 0/100 to 100/100 and more preferably from 25/100 to 70/100.

(2) Emulsification of toner composition liquid

[0118] The thus prepared toner composition liquid is emulsified in an aqueous medium including a surfactant and/or a particulate resin. Suitable materials for use as the aqueous medium include water. In addition, organic solvents which can be mixed with water can be added to water. Specific examples of such solvents include alcohols such as methanol, isopropanol, and ethylene glycol; dimethylformamide, tetrahydrofuran, cellosolves such as methyl cellosolve, lower ketones such as acetone and methyl ethyl ketone, etc.

[0119] The weight ratio of the aqueous medium to the toner composition liquid is generally from 50/100 to 2,000/100 and preferably from 100/100 to 1,000/100. When the added amount of the aqueous medium is too small, the toner composition liquid cannot be well dispersed, and thereby toner particles having a desired particle diameter cannot be prepared. Adding a large amount of aqueous medium is not economical.

[0120] The particulate resin to be included in the aqueous medium preferably has a glass transition temperature (Tg) of from 50 to 110 ˚C, more preferably from 50 to 90 ˚C, and even more preferably from 50 to 70 ˚C. When the glass transition temperature is too low, the high temperature preservability of the toner deteriorates, thereby causing a problem in that residual toner particles collected from image bearing members to be reused tend to be adhered to the inner surface of a feeding pipe through which the toner particles are fed to a developing device or a container, resulting in clogging of the pipe with the toner. In contrast, when the glass transition temperature is too high, the low temperature fixability of the toner deteriorates because the particulate resin decreases the adhesiveness of the toner to a receiving material.

[0121] In addition, the particulate resin preferably has a weight average molecular weight of from 4,000 to 100,000, and more preferably from 4,000 to 50,000. When the weight average molecular weight is too high, the low temperature fixability of the toner deteriorates because the particulate resin decreases the adhesiveness of the toner to a receiving material.

[0122] The particulate resin for use in the aqueous medium is not particularly limited, and any know resins (such as thermoplastic resins and thermosetting resins) can be used therefor as long as the resins can form aqueous dispersions. Suitable resins for use as the particulate resin include vinyl resins, polyurethane resins, epoxy resins, polyester resins, etc. This is because the resins can easily form aqueous dispersions in which spherical particles of the resins are dispersed. These resins can be used alone or in combination.

[0123] Specific examples of the vinyl resins include homopolymers and copolymers of one or more vinyl monomers such as styrene - (meth)acrylate copolymers, styrene - butadiene copolymers, (meth)acrylic acid - acrylate copolymers, styrene - acrylonitrile copolymers,styrene-maleic anhydride copolymers, styrene - (meth)acrylic acid copolymers, etc.

[0124] The particulate resin preferably has a volume average particle diameter of from 10 to 200 nm, and preferably from 20 to 80 nm when the particle diameter is measured with a light scattering photometer from Otsuka Electronics, Co., Ltd.

[0125] When the toner composition liquid is emulsified in an aqueous medium, a dispersant such as surfactants, particulate inorganic dispersants, particulate resin dispersants is preferably included in the aqueous medium.

[0126] Specific examples of the surfactants include anionic surfactants such as alkylbenzene sulfonic acid salts, α-olefin sulfonic acid salts, and phosphoric acid salts; cationic surfactants such as amine salts (e.g., alkyl amine salts, aminoalcohol fatty acid derivatives, polyamine fatty acid derivatives and imidazoline), and quaternary ammonium salts (e.g., alkyltrimethyl ammonium salts, dialkyldimethyl ammonium salts, alkyldimethyl benzyl ammonium salts, pyridinium salts, alkyl isoquinolinium salts and benzethonium chloride) ; nonionic surfactants such as fatty acid amide derivatives, polyhydric alcohol derivatives; and ampholytic surfactants such as alanine, dodecyldi(aminoethyl)glycin, di(octylaminoethyle)glycin, and N-alkyl-N,N-dimethylammonium betaine.

[0127] By using a fluorine-containing surfactant as the surfactant, good effects can be produced even when the added amount is small.

[0128] Specific examples of anionic surfactants having a fluoroalkyl group include fluoroalkyl carboxylic acids having from 2 to 10 carbon atoms and their metal salts, disodium perfluorooctanesulfonylglutamate, sodium 3-{omega-fluoroalkyl (C6-C11)oxy}-1-alkyl(C3-C4) sulfonate, sodium 3-{omega-fluoroalkanoyl (C6-C8)-N-ethylamino}-1-propanesulfo nate, fluoroalkyl(C11-C20) carboxylic acids and their metal salts, perfluoroalkyl (C7-C13) carboxylic acids and their metal salts, perfluoroalkyl (C4-C12) sulfonate and their metal salts, perfluorooctanesulfonic acid diethanol amides, N-propyl-N-(2-hydroxyethyl)perfluorooctanesulfone amide, perfluoroalkyl(C6-C10)sulfoneamidepropyltrimethylammonium salts,

salts of perfluoroalkyl (C6-C10)-N-ethylsulfonylglycin, monoperfluoroalkyl(C6-C16)ethylphosphates, etc.

[0129] Specific examples of the marketed products of such surfactants include SARFRON S-111, S-112 and S-113, which are manufactured by Asahi Glass Co., Ltd.; FLUORAD FC-93, FC-95, FC-98 and FC-129, which are manufactured by Sumitomo 3M Ltd.; UNIDYNE DS-101 and DS-102, which are manufactured by Daikin Industries, Ltd.; MEGAFACE F-110, F-120, F-113, F-191, F-812 and F-833 which are manufactured by Dainippon Ink and Chemicals, Inc.; ECTOP EF-102, 103, 104, 105, 112, 123A, 306A, 501, 201 and 204, which are manufactured by Tohchem Products Co., Ltd.; FUTARGENT F-100 and F150 manufactured by Neos; etc.

[0130] Specific examples of the cationic surfactants having a fluoroalkyl group, which can disperse an oil phase including toner constituents in water, include primary, secondary and tertiary aliphatic amines having a fluoroalkyl group, aliphatic quaternary ammonium salts such as perfluoroalkyl(C6-C10)sulfoneamidepropyltrimethylammonium salts, benzalkonium salts, benzetonium chloride, pyridinium salts, imidazolinium salts, etc. Specific examples of the marketed products thereof include SARFRON S-121 (from Asahi Glass Co., Ltd.); FLUORAD FC-135 (from Sumitomo 3M Ltd.); UNIDYNE DS-202 (from Daikin Industries, Ltd.); MEGAFACE F-150 and F-824 (from Dainippon Ink and Chemicals, Inc.); ECTOP EF-132 (from Tohchem Products Co., Ltd.); FUTARGENT F-300 (from Neos); etc.

[0131] Particulate resins are added to stabilize the toner particles formed in the aqueous medium and to prevent the wax from being present on the surface of the toner particles without being concealed. Specific examples of the particulate resins include particulate methyl methacrylate having a particle diameter of 1 μm or 3 μm, particulate polystyrene having a particle diameter of 0.5 μm or 2 μm, particulate styrene-acrylonitrile copolymers having a particle diameter of 1 μm (e.g., PB-200H from Kao Corp. , SPG from Soken Chemical & Engineering Co., Ltd., TECHNOPOLYMER SB from Sekisui Plastic Co., Ltd., SGP-3G from Soken Chemical & Engineering Co., Ltd., and MICROPEARL from Sekisui Fine Chemical Co., Ltd.). The particulate resins are preferably added so that part (i.e., 10 to 90%) of the surface of the toner particles is covered with the particulate resins.

[0132] Inorganic dispersants hardly soluble in water, such as tricalcium phosphate, calcium carbonate, titanium oxide, colloidal silica and hydroxyapatite, can also be used.

[0133] Further, it is preferable to stabilize the emulsion or dispersion using a polymer protection colloid in combination with the inorganic dispersants and particulate resins.

[0134] Specific examples of such protection colloids include polymers and copolymers prepared using monomers such as acids (e.g., acrylic acid, methacrylic acid, α-cyanoacrylic acid, α-cyanomethacrylic acid, itaconic acid, crotonic acid, fumaric acid, maleic acid and maleic anhydride), acrylic monomers having a hydroxyl group (e.g., β-hydroxyethyl acrylate, β -hydroxyethyl methacrylate, β-hydroxypropyl acrylate, β -hydroxypropyl methacrylate, γ-hydroxypropyl acrylate, γ -hydroxypropyl methacrylate, 3-chloro-2-hydroxypropyl acrylate, 3-chloro-2-hydroxypropyl methacrylate, diethyleneglycolmonoacrylic acid esters, diethyleneglycolmonomethacrylic acid esters, glycerinmonoacrylic acid esters, N-methylolacrylamide and N-methylolmethacrylamide), vinyl alcohol and its ethers (e.g., vinyl methyl ether, vinyl ethyl ether and vinyl propyl ether), esters of vinyl alcohol with a compound having a carboxyl group (i.e., vinyl acetate, vinyl propionate and vinyl butyrate); acrylic amides (e.g, acrylamide, methacrylamide and diacetoneacrylamide) and their methylol compounds, acid chlorides (e.g., acrylic acid chloride and methacrylic acid chloride), and monomers having a nitrogen atom or an alicyclic ring having a nitrogen atom (e.g., vinyl pyridine, vinyl pyrrolidone, vinyl imidazole and ethylene imine).

[0135] In addition, polymers such as polyoxyethylene compounds (e.g., polyoxyethylene, polyoxypropylene, polyoxyethylenealkyl amines, polyoxypropylenealkyl amines, polyoxyethylenealkyl amides, polyoxypropylenealkyl amides, polyoxyethylene nonylphenyl ethers, polyoxyethylene laurylphenyl ethers, polyoxyethylene stearylphenyl esters, and polyoxyethylene nonylphenyl esters); and cellulose compounds such as methyl cellulose, hydroxyethyl cellulose and hydroxypropyl cellulose, can also be used as the polymeric protective colloid.

[0136] Known dispersing machines can be used for emulsifying the toner composition liquid in an aqueous medium. Suitable dispersingmachines include low speed shear dispersingmachines, high speed shear dispersing machines, friction dispersing machines, high pressure jet dispersing machines, ultrasonic dispersing machines, etc. In order to prepare a dispersion having a particle diameter of from 2 to 20 μm, high speed shear dispersing machines are preferably used.

[0137] When high speed shear dispersing machines are used, the rotation number of the rotor is not particularly limited, but the rotation number is generally from 1,000 to 30,000 rpm, and preferably from 5,000 to 20,000. The dispersion time is not particularly limited. When a batch dispersing machines are used, the dispersion time is generally from 0.1 to 5 minutes. The dispersion temperature is preferably from 0 to 150 ˚C (under a pressure) and preferably from 40 to 98 ˚C.

(3) Reaction of prepolymer with amine

[0138] At the same time when the emulsion is prepared, an amine is added to the emulsion to react the amine with the prepolymer having an isocyanate group. This reaction accompanies crosslinking and/or molecular chain growth.

[0139] The reaction time is determined depending on the reactivity of the isocyanate group of the polyester prepolymer

with the amine used, and is generally from 10 minutes to 40 hours, and preferably from 2 to 24 hours. The reaction temperature is generally from 0 to 150 ˚C, and preferably from 40 to 98 ˚C.

[0140] In addition, known catalysts such as dibutyltin laurate and dioctyltin laurate can be used, if desired, for the reaction. As mentioned above, amines are typically used as the molecular chain growing agent and/or the crosslinking agent.

(4) Removal of solvent from reaction product

[0141] After the reaction, the organic solvent is removed from the reaction product to prepare a dispersion of toner particles. The toner particles are washed and then dried to prepare dry toner particles. In order to remove the organic solvent, the emulsion is gradually heated while the emulsion is agitated so as to have a laminar flow. In this case, it is preferable to remove the solvent in a certain temperature range while strongly agitating the emulsion, so that the resultant toner particles have a spindle form. When a dispersant, which can be dissolved in an acid or an alkali, such as calcium phosphate is used, it is preferable to dissolve the dispersant with hydrochloric acid to remove the dispersant from the toner particles, followed by washing with water. In addition, it is possible to remove such a dispersant by decomposing the dispersant using an enzyme.

(5) Addition of external additive

[0142] Then a charge controlling agent is fixed on the thus prepared toner particles and an external additive such as particulate inorganic materials (e.g., silica and titanium oxide) is added thereto. These materials can be added by a method using a known mixer or the like.

[0143] By using such a method, a toner having a small particle diameter and a sharp particle diameter distribution can be easily prepared. By controlling the agitation operation in the solvent removing process, the particle form of the toner particles can be easily changed from spherical forms to rugby-ball forms. In addition, the surface conditions of the toner particles can be controlled so as to have a surface of from smooth surface to rough surface like pickled plum.

[0144] Next, the methods for determining the properties of the toner mentioned above will be explained.

Melting point of release agent

[0145] The melting point of the release agent (paraffin wax) included in the toner is defined as the temperature at which the DSC curve of the wax has a maximum endothermic peak. A differential scanning calorimeter such as DSC-60 from Shimadzu Corporation is used as the measuring instrument. The temperature conditions are as follows.

Temperature conditions

[0146]

(First temperature rising operation)

Starting temperature: 20 ˚C
Temperature rising speed: 10 ˚C/min
End temperature: 150 ˚C
Retention time at end temperature: 0

(First cooling operation)

Cooling speed: 10 ˚C/min
End temperature: 20 ˚C
Retention time at end temperature: 0

(Second temperature rising operation)

Temperature rising speed: 10 ˚C/min
End temperature: 150 ˚C

[0147] The melting point of the release agent (paraffin wax) is determined from the endothermic peak in the second temperature rising process.

Endothermic quantity of endothermic peak specific to release agent

[0148] The endothermic quantity is calculated from the endothermic peak specific to the release agent when the release agent is subjected to a DSC analysis. A combination of TA-60WS and DSC-60 from Shimadzu Corporation is used as the measuring instrument. The measuring conditions are as follows.

Sample container: Aluminum pan with cap
Amount of sample: 5 mg
Reference sample: 10 mg of alumina contained in an aluminum pan
Atmosphere: Nitrogen (flow rate of 50 ml/min)
Temperature conditions

(First temperature rising operation)

Starting temperature: 20 ˚C
Temperature rising speed: 10 ˚C/min
End temperature: 150 ˚C
Retention time at end temperature: 0

(First cooling operation)

Cooling speed: 10 ˚C/min
End temperature: 20 ˚C
Retention time at end temperature: 0

(Second temperature rising operation)

Temperature rising speed: 10 ˚C/min
End temperature: 150 ˚C

[0149] The measurement data are analyzed by an analyzing software TA-60 version 1.52 from Shimadzu Corporation. The analysis is performed on the endothermic peak in the second temperature rising process. Specifically, when analyzing the endothermic peak, the data of the lower-side and higher-side base lines of the endothermic peak are input to calculate the endothermic quantity from the endothermic peak specific to the release agent using the software.

Particle diameter distribution of toner

[0150] The weight average particle diameter (D4), number average particle diameter (Dn) and particle diameter distribution of a toner are measured with a method using an instrument such as COULTER COUNTER TA-II and COULTER MULTISIZER II from Beckman Coulter Inc. Specifically, the procedure is as follows:

(1) a surfactant serving as a dispersant (preferably 0.1 to 5 ml of a 1 % aqueous solution of an alkylbenzenesulfonic acid salt), is added to 100 ml to 150 ml of an electrolyte such as 1 % aqueous solution of first class NaCl or ISOTON-II manufactured by Beckman Coulter Inc.;
(2) 2 to 20 mg of a sample to be measured is added into the electrolyte including the surfactant;
(3) the mixture is subjected to an ultrasonic dispersion treatment for about 1 to 3 minutes to disperse the sample in the electrolyte; and
(4) the volume-basis particle diameter distribution and number-basis particle diameter distribution of the sample are measured using the instrument in which the aperture is set to 100 μm to determine the weight average particle diameter (D4) and the number average particle diameter (Dn).

[0151] In the present invention, the following 13 channels are used:

(1) not less than 2.00 μm and less than 2.52 μm;
(2) not less than 2.52 μm and less than 3.17 μm;
(3) not less than 3.17 μm and less than 4.00 μm;
(4) not less than 4.00 μm and less than 5.04 μm;
(5) not less than 5.04 μm and less than 6.35 μm;

(6) not less than 6.35 μm and less than 8.00 μm;
(7) not less than 8.00 μm and less than 10.08 μm;
(8) not less than 10.08 μm and less than 12.70 μm;
(9) not less than 12.70 μm and less than 16.00 μm;
(10) not less than 16.00 μm and less than 20.20 μm;
(11) not less than 20.20 μm and less than 25.40 μm;
(12) not less than 25.40 μm and less than 32.00 μm; and
(13) not less than 32.00 μm and less than 40.30 μm.

[0152] Namely, particles having a particle diameter of from 2.00μ m to 40.30 μm are targeted.

Content of particles having particle diameter not greater than 2 μm

[0153] The content of particles having a particle diameter not greater than 2 μm in a toner is determined using a combination of a flow-type particle image analyzer FPIA-2100 and an analysis software FPIA-2100 DATA PROCESSING PROGRAM FOR FPIA VERSION 00-10, both from Sysmex Corp. The procedure of the measurement is as follows.

(1) at first 100 ml of water from which solid foreign materials have been removed, 0.5 ml of a surfactant (NEOGEN SC-A from Daiichi Kogyo Seiyaku Co., Ltd.), which serves as a dispersant and 0.1 to 0.5 g of a sample (i.e., toner) are mixed;
(2) the mixture is subjected to a supersonic dispersion treatment for about 3 minutes using a supersonic dispersion machine to prepare a dispersion including particles of the sample at a concentration of from 5,000 to 15,000 pieces/μl;
(3) the dispersion is passed through a detection area formed on a plate in the instrument; and
(4) the particles are optically detected by a CCD camera and then the shapes thereof are analyzed with an image analyzer, resulting in determination of the content of particles having a particle diameter of not greater than 2 μm in the sample (toner).

[0154] In this measurement, it is important to control the concentration so as to fall in the range of from 5, 000 to 15, 000 pieces/μl. In order to control the concentration, the added amount of the surfactant, and the added amount of the sample (i.e., toner) should be adjusted. Namely, the added amount of the surfactant should be determined depending on the hydrophobicity of the sample. Specifically, the sample has a high hydrophobicity, the added amount of the surfactant has to be increased. However, when the added amount of the surfactant is too large, the resultant dispersion of the sample includes bubbles and thereby noise is generated when the measurement is performed. With respect to the added amount of the sample, the larger particle diameter the sample (toner) has, the larger the added amount of the sample. When the sample has a particle diameter of from 3 to 7 μm, the added amount of the sample is from 0.1 to 0.5 g to control the concentration in the range of from 5,000 to 15,000 pieces/μl.

Torque

[0155] Several background arts have disclosed techniques of measuring the torque of toner. For example, JP-A 2004-177371 discloses a technique in that the fluidity of a toner powder including a resin and a pigment is measured by a method including the steps of entering a rotating cone-shaped rotor into the toner powder, and measuring the torque or load generated when the cone-shaped rotor moves in the toner powder, wherein the ratio (v/r) of the entering speed (v mm/min) of the rotor to the revolution (r rpm) of the rotor is controlled so as to be 2/1 to 20/1. In addition, JP-A 2004-177850 discloses a technique in that the fluidity of a toner powder including a resin and a pigment is measured by a method including the steps of entering a rotating cone-shaped rotor into the toner powder, and measuring the torque or load generated when the cone-shaped rotor moves in the toner powder. Further, JP-A 2006-78257 discloses an improved technique of measuring the torque of toner with small measurement error, which is used for the present application.

[0156] As a result of the present inventors' investigation of measuring the torque of toner, it is found that the torque of toner can be precisely measured by the method mentioned above, and the torque is closely related to the cleaning properties of the toner. Specifically, in a toner having a large torque, which is measured by the above-mentioned method, the toner particles thereof have large interaction with each other under a pressed condition. Therefore, in a cleaning process in which toner particles remaining on a photoreceptor are removed with a cleaning blade, the toner particles blocked by the blade are aggregated and form a toner layer. Accordingly, the remaining toner particles are blocked with the toner layer as well as the blade. Therefore, the amount of toner particles passing though the nip between the blade and the surface of the photoreceptor decreases. Thus, the toner has a good cleanability.

[0157] When the toner has a torque less than 1.2 mNm, the cleanability of the toner deteriorates. In contrast, when

the toner has a torque greater than 2.0 mNm, a clogging problem such that a toner feeding pipe is clogged with the toner tends to occur. Therefore, the torque should be controlled so as to be from 1.2 mNm to 2.0 mNm, and preferably from 1.4 to 2.0 mNm.

[0158] As mentioned above, the method for measuring the torque of toner in the present application is the same as disclosed in JP-A 2006-78257. Specifically, in the method, a rotating cone-shaped rotor is moved up and down to enter the rotor into the toner layer or pull the rotor from the toner layer. In this case, the torque and load applied to the rotor and the container in which the toner is contained are measured. The torque and load are related to the fluidity of the toner.

[0159] The apex angle of the cone-shaped rotor is preferably 60 degree. The rotor preferably has a relatively long length such that the entire of the rotor is not sunk into the toner layer (i.e., the surface of the rotor can be observed without being covered by the toner layer), and the length of the rotor is 300 mm in this application. In addition, the surface of the rotor preferably has grooves so that friction between toner particles present in the recessed portions of the grooves and other toner particles in the vicinity of the toner particles in the recessed portions can be determined instead of the friction between the toner particles in the recessed portions and the surface of the recessed portions of the rotor. The shape of the grooves is not particularly limited, but the shape of the rotor is preferably determined such that the contact between toner particles and the surface of the rotor is minimized.

[0160] FIGS. 2A and 2B illustrate an example of the cone-shaped rotor. The rotor has grooves which extend from the top of the cone to the bottom of the cone. As illustrated in FIG. 2B, the grooves have a v-form, i.e., the surface of the cone has a shape like teeth of a saw. In this rotor, the rotor frictionally contacts the toner particles only at the projected portions of the grooves, and the surfaces of the grooves are hardly frictionally contacted with the toner particles. This is because the toner particles present in the recessed portions of the grooves hardly move and are frictionally contacted with the toner particles in the vicinity thereof. The material constituting the rotor is not particularly limited as long as the material is hard and has good stability (i.e., hardly changes its quality), good processability and less chargeability. In the present application, the rotor is made of copper.

[0161] The torque and the load change depending on the revolution and entering speed of the rotor. In the present application, the revolution and entering speed of the rotor are decreased so that the contact between toner particles can be precisely measured. Specifically, the revolution and entering speed of the rotor are set as follows.

Revolution of the rotor: 1 rpm
Entering speed of the rotor: 5 mm/min

[0162] FIG. 1 is a schematic view illustrating an example of the instrument for measuring the torque of toner.

[0163] Referring to FIG. 1, an instrument 100 includes a torque meter 1, a cone-shaped rotor 2, a container configured to contain a sample (i.e., toner) therein, a load cell 4 conf igured to measure the load applied to the container 3, a sample table 5 on which the container 3 is set, an elevator 6 configured to move the torque meter 1 up and down, and a position detector 7 configured to determine the position of the rotor 2. The rotor 2 is connected with a shaft 8 of the torque meter 1 to be fixed with the torque meter 1. When the torque meter 1 is moved down by the elevator 6, the rotor 2 enters into the toner layer in the container 3 while rotating, which is set at the center of the table 5. The torque applied to the rotor 2 is measured with the torque meter 1, and the load applied to the container 3 is measured with the load cell 4. The moving distance of the rotor 2 is measured with the position detector 7. The instrument is not limited to the instrument 100, and for example, an instrument in which the container 3 is moved up and down by an elevator can also be used.

[0164] FIGS. 3A-3C illustrates other examples of the cone-shaped rotor. The rotors illustrated in FIGS. 3A and 3B have eight and four grooves on the surface thereof, respectively. The rotor illustrated in FIG. 3C has a wider apex angle than the rotor illustrated in FIG. 2A.

[0165] The material constituting the container 3 is not particularly limited, but an electroconductive material is preferably used therefor to prevent charging of the container and the sample, which seriously influences the measurement of the torque. In addition, the inner surface of the container 3 is preferably a mirror finished surface so that the inner surface is hardly contaminated with samples. The dimension of the container 3 is an important factor. When the container 3 is relatively small, the rotation of the rotor 2 is influenced by the inner surface of the container 3. Therefore, it is preferable that the diameter of the container 3 is relatively large compared to the diameter of the rotor 2. In this application, the container 3 is an aluminum cylinder having an inside diameter of 60 mm and a height of 30 mm.

[0166] The torque meter 1 is preferably a noncontact-type high sensitive torque meter. The load cell 4 preferably has a wide measurable load range and a wide resolution. Specific examples of the position detector 7 include linear scales in which the detected positional information is changed to a control signal for canceling the deviance between the current position and a predetermined position, and the control signal is sent to a driving circuit of a motor of the elevator; and displacement sensors using light. The accuracy of the position detector 7 is preferably 0.1 mm or less (better). Specific examples of the elevator 6 include high precision elevators using a servomotor or a stepping motor.

[0167] FIG. 4 illustrates another example of the instrument for measuring the torque of toner, which has a pressing function.

[0168] Referring to FIG. 4, an instrument 200 includes a measuring zone 10 and a pressing zone 20. The measuring zone 10 includes the torque meter 1, the cone-shaped rotor 2 which is fixedly connected with the shaft 8 of the torque meter 1, the container 3, the load cell 4, and a first elevating stage 9 configured to move the container 3 up and down. The pressing zone 20 includes a weight 21 configured to press a piston 22, which presses the toner in a container 3'. Numerals 24 and 25 denote a vibrator and a second elevating stage.

[0169] In the pressing zone 20, the container 3' is the same as the container 3 and is an aluminum container having an inside diameter of 60 mm and a height of 30 mm. The weight 21 is a cylindrical weight having a weight of 585g and a diameter of 60 mm.

[0170] The procedure for preparing the toner layer to be set on the first elevating stage 9 is as follows. At first, a sample (toner) is fed into the container 3' so as to have a height of 23 mm, and the container 3' is set on the vibrator 24. The container 3' is vibrated with the vibrator 24 so that the toner layer has a uniform thickness. Next, the container 3' is moved up with the second elevating stage 25, so that the toner layer in the container 3' is contacted with the piston 22. Thecontainer is further moved up so that the weight 21 is separated from a support plate 23, thereby pressing the toner layer with the piston to which a weight is applied. In this regard, a load of 585g, which is the total weight of the weight and the piston, is applied to the toner, and the pressing operation is performed for 60 seconds. In this regard, since the piston has a diameter of 6 cm and an area of 28.26 cm^2, a pressure of 20.7 gf/cm^2 (i.e., 2028.6 Pa) is applied to the toner. Next, the elevating stage 25 is moved down so that the toner layer is separated from the piston 22.

[0171] The material constituting the piston is not particularly limited, but the surface of the piston to be contacted with the toner is preferably a smooth surface. Therefore, the material is preferably hard and stable (i.e., hardly changes its property), and has a good processability. In addition, it is necessary for the material not to charge, and therefore the material is preferably electroconductive. From this viewpoint, copper is used for the piston 22.

[0172] When measuring the torque and the load, the rotor 2 is entered into the toner layer at a predetermined speed while rotated at a predetermined revolution. The direction of the rotation of the rotor is not particularly limited. The distance (depth) by which the rotor 2 is entered into the toner layer is preferably as long as possible so that the measured data have good reproducibility. As a result of the present inventors' study, the distance is determined to be 20 mm. Namely, the torque is measured when the rotor 2 is entered into the toner layer by 20 mm in depth.

[0173] The procedure for measuring the torque using the instrument 200 illustrated in FIG. 4 is as follows.

1. A sample (toner) is fed into the container 3'.
2. The toner is pressed with the piston 22 which is pressed by the weight 21.
3. The container 3' (i.e., container 3) containing the toner layer is set on the first elevating stage 9 of the measuring zone.
4. The first elevating stage 9 is moved up so that the rotor 2, which is rotated, is entered into the toner layer in the container 3 while measuring the torque.
5. When the rotor 2 reaches a predetermined position, the elevating operation of the first elevating stage 9 is stopped.
6. The elevating table is moved down so that the rotor 2 is pulled out of the toner layer.
7. When the rotor 2 is separated from the surface of the toner layer, the elevating operation of the first elevating stage 9 is stopped and the rotation of the rotor is also stopped.

Shape factors SF-1 and SF-2

[0174] FIGS. 5 and 6 are schematic views for explaining the first and second shape factors SF-1 and SF-2, respectively.

[0175] As illustrated in FIG. 5, the first shape factor SF-1 represents the degree of the roundness of a toner and is defined by the following equation (1):

$$SF\text{-}1 = \{(MXLNG)^2 / (AREA)\} \times (100\pi/4) \qquad (1)$$

wherein MXLNG represents a diameter of the circle circumscribing the image of a toner particle, which image is obtained by observing the toner particle with a microscope; and AREA represents the area of the image.

[0176] When the SF-1 is 100, the toner particle has a true spherical form. As the SF-1 increases, the shape of the toner particles approaches irregular forms.

[0177] As illustrated in FIG. 6, the second shape factor SF-2 represents the degree of the concavity and convexity of a toner particle, and is defined by the following equation (2):

$$SF\text{-}2 = \{(PERI)^2 / (AREA)\} \times (100/4\pi) \qquad (2)$$

wherein PERI represents the peripheral length of the image of a toner particle observed by a microscope; and AREA represents the area of the image.

[0178] When the SF-2 approaches 100, the toner particles have a smooth surface (i.e., the toner has few concavity and convexity) . As the SF-2 increases, the toner particles have a rougher surface.

[0179] The first and second shape factors SF-1 and SF-2 are determined by the following method:

(1) particles of a toner are photographed using a scanning electron microscope (S-800, manufactured by Hitachi Ltd.); and
(2) photograph images of one hundred toner particles are analyzed using an image analyzer (LUZEX 3 manufactured by Nireco Corp.) to determine the first and second shape factors SF-1 and SF-2.

Circularity

[0180] The circularity of a toner is measured with a combination of a flow-type particle image analyzer FPIA-2100 and an analysis software FPIA-2100 DATA PROCESSING PROGRAM FOR FPIA VERSION 00-10, both from Sysmex Corp. The procedure is mentioned above. In the analysis process, the particles having a particle diameter of from 2 μm to 400 μm are targeted.

Content of particles having a particle diameter of not greater than 2 μm

[0181] The method for determining the content of particles having a particle diameter of not greater than 2 μm in a toner is mentioned above.

Molecular weight of resin

[0182] In the present application, the molecular weight distribution of a resin was determined by gel permeation chromatography (GPC). The method is as follows.

1) the column is allowed to settle in a chamber heated to 40 ˚C so as to be stabilized;
2) tetrahydrofuran (THF) is passed through the column thus heated to 40 ˚C at a flow rate of 1 ml/min; and
3) then 50 to 200 μl of a tetrahydrofuran(THF) solution of a resin having a solid content of from 0.05 to 0.6% by weight is injected to the column to obtain a molecular distribution curve of the resin.

[0183] The THF resin solution of the resin was prepared by the following method:

i) the resin is dissolved in tetrahydrofuran to prepare a THF solution of the resin;
ii) the resin solution (or dispersion) is subjected to filtering using a filter having openings with a diameter of 0.45 μm for use in liquid chromatography to remove THF-insoluble components therefrom.

[0184] The molecular weight distribution of the resin is determined using a working curve, by which the relationship between weight and GPC counts is illustrated and which is previously prepared using monodisperse polystyrenes. Specific examples of the molecular weights of the monodisperse polystyrenes include 6×10^2, 2.1×10^3, 4×10^3, 1.75×10^4, 1.1×10^5, 3.9×10^5, 8.6×10^5, 2×10^6, and 4.48×10^6. The monodisperse polystyrenes are available from Pressure Chemical Co., or Tosoh Corp. It is preferable to prepare a working curve using ten or more kinds of monodisperse polystyrenes. In measurements, it is preferable to use a RI (refractive index) detector as the detector.

Acid value of resin

[0185] The acid value of a resin is determined by the method described in JIS K0070-1992.

[0186] At first, about 0.5 g of a sample (resin), which is precisely measured, is mixed with 120 ml of toluene. The mixture is agitated for about 10 hours at room temperature (23 ˚C), and 30 ml of ethanol is added thereto to prepare a sample solution. The sample solution is subjected to titration using a N/10 alcohol solution of potassium hydroxide. The acid value (AV) of the sample is determined by the following equation.

$$AV = (KOH \times N \times 56.1)/W$$

wherein KOH represents the amount (ml) of KOH consumed in the titration, N represents the factor of N/10 potassium hydroxide, and W represents the precise weight of the sample.

Hydroxyl value of resin

[0187] The instrument and the measurement conditions are the same as those in the above-mentioned acid value measurement method. The procedure is as follows.

[0188] At first, about 0.5 g of a sample, which is precisely measured, is mixed with 5 ml of an acetylizing agent. Then the mixture is heated in a temperature range of 100 ± 0.5 ˚C using a bath. After one or two hours, the flask is drawn from the bath. After cooling the flask, water is added thereto and the mixture is shaken to decompose acetic anhydride. Further, in order to completely decompose acetic anhydride, the flask is heated for 10 minutes or more using the bath. After cooling the flask, the inner surface of the flask is well washed with an organic solvent. This liquid is subjected to a potentiometric titration treatment using a N/2 ethyl alcohol solution of potassiumhydroxide to determine the hydroxyl value of the sample. The measurement method is based on JIS K0070-1966.

Glass transition temperature (Tg)

[0189] The method for measuring the glass transition temperature of a resin is measured by an instrument TG-DSC system TAS-100 manufactured by RIGAKU CORPORATION. The procedure for measurements of glass transition temperature is as follows:

1) about 10 mg of a sample is contained in an aluminum container, and the container is set on a holder unit;
2) the holder unit is set in an electrical furnace, and the sample is heated from room temperature to 150 ˚C at a temperature rising speed of 10 ˚C/min;
3) after the sample is allowed to settle at 150 ˚C for 10 minutes, the sample is cooled to room temperature; and
4) after the sample is allowed to settle at room temperature for 10 minutes, the sample is heated again from room temperature to 150 ˚C in a nitrogen atmosphere at a temperature rising speed of 10 ˚C/min to perform a DSC measurement.

[0190] The glass transition temperature of the sample is determined using an analysis system of the TAS-100 system. Namely, the glass transition temperature is defined as the contact point between the tangent line of the endothermic curve at the temperatures near the glass transition temperature and the base line of the DSC curve.

Toner concentration

[0191] When the toner of the present invention is used as a two-component developer for full color image forming apparatuses, the concentration of the toner in the developer is preferably from 3 to 12% by weight to produce images with a proper image density. The concentration of toner in a two component developer, which is a mixture of the toner and a carrier, is determined such that the toner particles cover the surface of the carrier particles in a ratio of not greater than 100%. In this case, the particles of the toner and particles of the carrier are well contacted, and thereby the toner is well charged by the carrier. When the toner concentration is too high, a problem in that the toner constitutional materials having a low melting point such as waxes and resins are adhered to the surface of the carrier, resulting in deterioration of chargeability of the carrier occurs.

[0192] Any known materials conventionally used for the carrier can be used as the carrier.

[0193] Next, the process cartridge of the present invention will be explained.

[0194] The process cartridge is detachably set in an image forming apparatus as a unit, and includes at least an image bearing member configured to bear an electrostatic latent image thereon, and a developing device configured to develop the electrostatic image with a developer including the toner of the present invention. The process cartridge can optionally include other devices such as charging devices configured to charge the image bearing member, light irradiating devices configured to irradiate the charged image bearing member with light to form an electrostatic image thereon, transfer devices configured to transfer a toner image on the image bearing member to a receiving material, cleaning devices configured to clean the surface of the image bearing member and discharging devices configured to discharge the charges remaining on the image bearing member.

[0195] The developing device of the process cartridge includes at least a developer containing portion containing a

developer including the toner mentioned above, and a developer bearing member configured to bear the developer thereon to feed the developer to the image bearing member.

[0196] An example of the process cartridge of the present invention is illustrated in FIG. 8. The process cartridge includes a photoreceptor 101 serving as an image bearing member, a charging device 102, a developing device having a developer bearing member 104, and a cleaning device 107. In FIG. 8, numerals 103, 105 and 108 denote imagewise light emitted by a light irradiating device, a receiving material, and a transfer roller serving a as a transfer device. Specific examples of the photoreceptor 101, the light irradiating device (103) and the charging device 102 include known devices for use in conventional image forming apparatuses and process cartridges.

[0197] Having generally described this invention, further understanding can be obtained by reference to certain specific examples which are provided herein for the purpose of illustration only and are not intended to be limiting. In the descriptions in the following examples, the numbers represent weight ratios in parts, unless otherwise specified.

EXAMPLES

Example 1

Preparation of resin dispersion

[0198] In a reaction vessel equipped with a stirrer and a thermometer, 683 parts of water, 11 parts of a sodium salt of sulfate of an ethylene oxide adduct of methacrylic acid (ELEMINOL RS-30 from Sanyo Chemical Industries Ltd.), 83 parts of styrene, 83 parts of methacrylic acid, 110 parts of butyl acrylate, and 1 part of ammonium persulfate were mixed. The mixture was agitated for 30 minutes while the stirrer was rotated at a revolution of 3,800 rpm. As a result, a milk white emulsion was prepared. Then the emulsion was heated to 75 ˚C to react the monomers for 4 hours.

[0199] Further, 30 parts of a 1 % aqueous solution of ammonium persulfate was added thereto, and the mixture was aged for 6 hours at 75 ˚C. Thus, an aqueous dispersion of a vinyl resin (i.e., a copolymer of styrene / methacrylic acid / butyl acrylate / sodium salt of sulfate of ethylene oxide adduct of methacrylic acid, hereinafter referred to as particulate resin dispersion (1)) was prepared.

[0200] The volume average particle diameter of the particles in the particulate resin dispersion (1), which was measured with a laser diffraction/scattering particle diameter measuring instrument LA-920 from Horiba Ltd., was 110 nm. In addition, part of the particulate resin dispersion (1) was dried to prepare a solid of the vinyl resin. It was confirmed that the vinyl resin has a glass transition temperature of 58 ˚C and a weight average molecular weight of 130,000.

Preparation of aqueous phase liquid

[0201] In a reaction vessel equipped with a stirrer, 990 parts of water, 83 parts of the particulate resin dispersion (1) prepared above, 37 parts of an aqueous solution of a sodium salt of dodecyldiphenyletherdisulfonic acid (ELEMINOL MON-7 from Sanyo Chemical Industries Ltd., solid content of 48.3 %), and 90 parts of ethyl acetate were mixed while agitated. As a result, a milk white liquid (hereinafter referred to as an aqueous phase liquid (1)) was prepared.

Preparation of low molecular weight polyester resin

[0202] The following components were contained in a reaction vessel equipped with a condenser, a stirrer and a nitrogen feed pipe and the mixture was subjected to a polycondensation reaction for 7 hours at 230 ˚C under a normal pressure.

[0203] Ethylene oxide (2 mole) adduct of

bisphenol A	724 parts
Terephthalic acid	276 parts

[0204] Then the reaction was further continued for 5 hours under a reduced pressure of from 1332 to 1998 Pa (10 to 15 mmHg).

[0205] Thus, a low molecular weight polyester resin (1) (i.e., unmodifiedpolyester resin) was prepared. It was confirmed that the low molecular weight polyester resin (1) has a number average molecular weight of 2,300, a weight average molecular weight of 6, 700, a peak molecular weight of 3, 800, a glass transition temperature (Tg) of 43 ˚C, and an acid value of 4 mgKOH/g.

Preparation of polyester prepolymer

[0206] The following components were contained in a reaction vessel equipped with a condenser, a stirrer and a nitrogen feed pipe, and the mixture was reacted for 8 hours at 230 ˚C under a normal pressure.

Ethylene oxide (2 mole) adduct of bisphenol A	682 parts
Propylene oxide (2 mole) adduct of bisphenol A	81 parts
Terephthalic acid	283 parts
Trimellitic anhydride	22 parts
Dibutyl tin oxide	2 parts

[0207] Then the reaction was further continued for 5 hours under a reduced pressure of from 1332 to 1998 Pa (10 to 15 mmHg). Thus, an intermediate polyester resin (1) was prepared. The intermediate polyester (1) has a number average molecular weight of 2,200, a weight average molecular weight of 9,700, a peak molecular weight of 3, 000, a glass transition temperature (Tg) of 54 ˚C, an acid value of 0.5 mgKOH/g and a hydroxyl value of 52 mgKOH/g.

[0208] In a reaction vessel equipped with a condenser, a stirrer and a nitrogen feed pipe, 410 parts of the intermediate polyester resin (1), 89 parts of isophorone diisocyanate and 500 parts of ethyl acetate were mixed and the mixture was heated for 5 hours at 100 ˚C to perform the reaction. Thus, a polyester prepolymer (1) having an isocyanate group was prepared. It was confirmed that the polyester prepolymer (1) includes free isocyanate in an amount of 1.53% by weight based on the total weight of the prepolymer.

Synthesis of ketimine compound

[0209] In a reaction vessel equipped with a stirrer and a thermometer, 170 parts of isophorone diamine and 75 parts of methyl ethyl ketone were mixed and reacted for 4.5 hours at 50 ˚C to prepare a ketimine compound (1). The ketimine compound (1) has an amine value of 417 mgKOH/g.

Preparation of master batch

[0210] The following components were mixed using a HENSCHEL MIXER (trademark) mixer from Mitsui Mining Co., Ltd.

Water	1200 parts
Carbon black (PRINTEX 35 from Degussa A.G., having DBP oil absorption of 42 ml/100mg, and pH of 9.5)	540 parts
Polyester resin	1200 parts

[0211] The mixture was kneaded for 1 hour at 130 ˚C using a two roll mill. Then the kneaded mixture was cooled by rolling, followed by pulverization. Thus, a master batch (1) was prepared.

Preparation of oil phase liquid

[0212] In a reaction vessel equipped with a stirrer and a thermometer, 378 parts of the low molecular weight polyester resin (1), 100 parts of a paraffin wax having a melting point of 70 ˚C, and 947 parts of ethyl acetate were mixed and the mixture was heated to 80 ˚C while agitated. After the mixture was heated at 80 ˚C for 5 hours, the mixture was cooled to 30 ˚C over 1 hour. Then 500 parts of the master batch (1), 30 parts of a montmorillonite in which part of interlayer ions is modified by organic ions, and 500 parts of ethyl acetate were added to the vessel, and the mixture was agitated for 1 hour to prepare a raw material dispersion (1).

[0213] Then 1,324 parts of the raw material dispersion (1) was subjected to a dispersion treatment using a bead mill (ULTRAVISCOMILL from Aimex Co., Ltd.). The dispersing conditions were as follows.

Liquid feeding speed: 1 kg/hour
Peripheral speed of disc: 6 m/sec
Dispersion media: zirconia beads with a diameter of 0.5 mm
Filling factor of beads: 80 % by volume
Repeat number of dispersing operation: 3 times (3 passes)

[0214] Next, 1324 parts of 65 % ethyl acetate solution of the low molecular weight polyester resin (1) prepared above and the particulate inorganic material (1) were added thereto. The mixture was subjected to the dispersion treatment using the bead mill. The dispersion conditions are the same as those mentioned above except that the dispersion operation was performed twice.

[0215] The thus prepared pigment/wax dispersion (1) had a solid content of 50%.

Emulsification

[0216] Then the following components were fed in a vessel.

Pigment/wax dispersion (1) prepared above	749 parts
Polyester prepolymer (1) prepared above	115 parts
Ketimine compound (1) prepared above	2.9 parts

[0217] The components were mixed for 2 minutes using a TK HOMOMIXER (trademark) mixer from Tokushu Kika Kogyo K.K. at a revolution of 5,000 rpm. Thus, an oil phase liquid (1) (i.e., a toner composition liquid) was prepared.

[0218] Then 1, 200 parts of the aqueous phase liquid (1) was added to the oil phase liquid (1), and the mixture was mixed for 25 minutes using the TK HOMOMIXER mixer at a revolution of 13, 000 rpm. Thus, an emulsion (1) was prepared.

Solvent removal

[0219] The emulsion was fed into a vessel equipped with a stirrer and a thermometer, and heated for 7 hours at 30 ˚C to remove the solvent therefrom. The thus prepared dispersion was further aged for 7 hours at 45 ˚C. Thus, a dispersion (1) was prepared.

Washing and drying

[0220] One hundred (100) parts of the dispersion (1) was filtered under a reduced pressure.

[0221] Then the wet cake was mixed with 100 parts of ion-exchange water and the mixture was agitated for 10 minutes with a TK HOMOMIXER (TRADEMARK) mixer at a revolution of 12,000 rpm, followed by filtration. Thus, a wet cake (a) was prepared.

[0222] The thus prepared wet cake (a) was mixed with 100 parts of a 10 % sodium hydroxide and the mixture was agitated for 10 minutes with the TK HOMOMIXER (TRADEMARK) mixer at a revolution of 12,000 rpm, followed by filtration. Thus, a wet cake (b) was prepared.

[0223] The thus prepared wet cake (b) was mixed with 100 parts of a 10 % hydrochloric acid and the mixture was agitated for 10 minutes with the TK HOMOMIXER (TRADEMARK) mixer at a revolution of 12,000 rpm, followed by filtration. Thus, a wet cake (c) was prepared.

[0224] Then the wet cake (c) was mixed with 300 parts of ion-exchange water and the mixture was agitated for 10 minutes with the TK HOMOMIXER (TRADEMARK) mixer at a revolution of 12, 000 rpm, followed by filtration. This operation was repeated twice. Thus, a wet cake (1) was prepared.

[0225] The wet cake (1) was dried for 48 hours at 45 ˚C using a circulation air drier, followed by screening with a sieve having openings of 75 μm.

[0226] Thus, toner particles (1) were prepared.

Addition of external additive

[0227] One hundred (100) parts of the toner particles (1) were mixed with 1 part of a hydrophobized silica and 1 part of a hydrophobized titanium oxide using a HENSCHEL MIXER mixer.

[0228] Thus, a toner of Example 1 was prepared.

Comparative Example 1

[0229] The procedure for preparation of the toner in Example 1 was repeated except that the added amount of the modified montmorillonite was changed from 30 parts to 0 part.

[0230] Thus, a toner of Comparative Example 1 was prepared.

Comparative Example 2

[0231] The procedure for preparation of the toner in Example 1 was repeated except that the paraffin wax was replaced with 100 parts of a carnauba wax having a melting point of 83 ˚C.

[0232] Thus, a toner of Comparative Example 2 was prepared.

Comparative Example 3

[0233] The procedure for preparation of the toner in Example 1 was repeated except that the added amount of the modified montmorillonite was changed from 30 parts to 0 part, and the paraffin wax was replaced with 100 parts of a paraffin wax having a melting point of 110 ˚C.

[0234] Thus, a toner of Comparative Example 3 was prepared.

Comparative Example 4

[0235] The procedure for preparation of the toner in Example 1 was repeated except that the added amount of the modified montmorillonite was changed from 30 parts to 0 part, and the paraffin wax was replaced with 100 parts of a carnauba wax having a melting point of 83 ˚C.

[0236] Thus, a toner of Comparative Example 4 was prepared.

Example 2

[0237] The procedure for preparation of the toner in Example 1 was repeated except that the added amount of the modified montmorillonite was changed from 30 parts to 48 parts.

[0238] Thus, a toner of Example 2 was prepared.

Example 3

[0239] The procedure for preparation of the toner in Example 1 was repeated except that the added amount of the modified montmorillonite was changed from 30 parts to 12 parts.

[0240] Thus, a toner of Example 3 was prepared.

Example 4

[0241] The procedure for preparation of the toner in Example 1 was repeated except that the added amount of the paraffin was changed from 100 parts to 150 parts.

[0242] Thus, a toner of Example 4 was prepared.

Example 5

[0243] The procedure for preparation of the toner in Example 1 was repeated except that the added amount of the paraffin was changed from 100 parts to 75 parts.

[0244] Thus, a toner of Example 5 was prepared.

Example 6

[0245] The procedure for preparation of the toner in Example 1 was repeated except that the low molecular weight polyester resin (1) was replaced with a low molecular weight polyester resin (2), which was prepared as follows.

Preparation of low molecular weight polyester (2)

[0246] The following components were contained in a reaction vessel equipped with a condenser, a stirrer and a nitrogen feed pipe and the mixture was subjected to a polycondensation reaction for 10 hours at 210 ˚C under a normal pressure.

Ethylene oxide (2 mole) adduct of bisphenol A	690 parts
Terephthalic acid	335 parts

[0247] Then the reaction was further continued for 5 hours under a reduced pressure of from 1332 to 1998 Pa (10 to 15 mmHg) while removing water. Next, the reaction product was cooled.

[0248] Thus, a low molecular weight polyester resin (2) was prepared. It was confirmed that the low molecular weight polyester resin (1) has a weight average molecular weight of 6, 000, a glass transition temperature (Tg) of 55 ˚C, and an acid value of 20 mgKOH/g.

[0249] Thus, a toner of Example 6 was prepared.

Example 7

[0250] The procedure for preparation of the toner in Example 1 was repeated except that the revolution of the HOMOMIXER mixer was increased to prepare a toner having a relatively small average particle diameter.

[0251] Thus, a toner of Example 7 was prepared.

[0252] The following properties of the thus prepared toners are shown in Table 1.

1. Torque (TOR) (i.e., fluidity of toner)
   The torque of each toner was measured with the above-mentioned method using the instrument illustrated in FIG. 4 to evaluate the fluidity of the toner.
2. Average circularity (AC)
3. Shape factors SF-1 and SF-2
4. Weight average particle diameter (D4)
5. Ratio (D4/Dn) of weight average particle diameter (D4) to number average particle diameter (Dn)
6. Endothermic quantity of peak specific to wax determined by DSC analysis (EQ)
7. Glass transition temperature (Tg)
8. Content of particles having a particle diameter of not greater than 2 μm ($CP_{\leq 2}$) in units of % by number

[0253] The methods for measuring the properties are mentioned above.

Table 1

	TOR (mNm)	AC	SF-1	SF-2	D4 (μm)	D4/Dn	EQ (J/g)	Tg (˚C)	$CP_{\leq 2}$ (%N)
Ex. 1	1.7	0.960	149	120	5.8	1.20	3.8	52	6
Ex. 2	1.9	0.945	156	138	5.8	1.24	3.8	49	8
Ex. 3	1.5	0.970	133	113	5.8	1.22	3.8	49	7
Ex. 4	1.8	0.961	146	122	5.7	1.20	6.0	50	7
Ex. 5	1.6	0.960	147	124	5.8	1.20	3.0	50	6
Ex. 6	1.6	0.962	146	118	5.6	1.22	4.0	58	8
Ex. 7	1.6	0.961	152	126	5.8	1.21	3.7	49	8
Comp. Ex. 1	1.3	0.986	128	109	5.9	1.21	4.0	48	8
Comp. Ex. 2	1.5	0.962	146	119	5.8	1.17	4.2	50	6
Comp. Ex. 3	1.2	0.988	126	108	5.7	1.15	3.8	50	7
Comp. Ex. 4	1.1	0.987	128	108	5.8	1.19	4.1	50	8

Preparation of two component developer

[0254] Each of the toners prepared above was mixed with a carrier, which was prepared by the below-mentioned method, while changing the concentration of the toner so as to be 3% by weight, and 12% by weight based on the total weight of the developer. The mixture was agitated for 10 minutes using a TURBULA mixer, which was operated at the maximum power. The weight of each developer was 1 kg.

[0255] The method for preparing the carrier is as follows.

[0256] The following components were mixed for 10 minutes with a HOMOMIXER mixer from Tokushu Kika Kogyo K. K. to prepare a coating liquid.

Solution of acrylic resin (solid content of 50% by weight) 21.0 parts

(continued)

Solution of guanamine (solid content of 70% by weight)	6.4 parts
Particulate alumina (average particle diameter of 0.3 μm, volume resistivity of 10^{14} Ω · cm)	7.6 parts
Solution of silicone resin (SR2410 from Dow Corning Toray Silicone Co., Ltd., solid content of 23% by weight)	65.0 parts
Aminosilane (SH6020 from Dow Corning Toray Silicone Co., Ltd., solid content of 100% by weight)	0.3 parts
Toluene	60 parts
Butyl cellosolve	60 parts

[0257] The surface of a calcined ferrite powder, which serves as a core material of the carrier and has a formula of $(MgO)_{1.8}$ $(MnO)_{49.5}$ $(Fe_2O_3)_{48.0}$, was coated with the above-prepared coating liquid using a SPIRA COTA coater from Okada Seiko Co., Ltd. , followed by drying. The thickness of the resultant cover film formed on the carrier particles was 0.15 μm in average. The thus prepared coated carrier particles were then calcined for 1 hour at 150 ˚C using an electric furnace, followed by cooling. The calcined carrier was then filtered using a screen having openings of 106 μm. Thus, a carrier 1 was prepared.

[0258] The thickness of the cover film was determined by observing cross sections of the carrier particles with a transmission electronic microscope and averaging the thickness data.

[0259] Each of the toners and developers prepared above was evaluated as follows.

1. Cleanability of toner

[0260] The procedure for evaluating the cleanability of a toner is as follows.

(1) The toners and an image forming apparatus (IMAGIO NEO C600 from Ricoh Co., Ltd.) serving as an evaluation machine were allowed to settle for one day in a chamber controlled at 25˚C and 50%RH.
(2) The process cartridge of the image forming apparatus was detached therefrom, and the toner included in the developer in the developing device of the process cartridge was removed so that only carrier is contained in the developing device.
(3) Twenty eight (28) grams of a toner was mixed with the carrier to prepare 400 g of a developer including the toner at a concentration of 7% by weight.
(4) The process cartridge was attached to the image forming apparatus and the developing device was idled for 5 minutes, wherein the developing sleeve was rotated at a linear speed of 300 mm/s.
(5) The developing sleeve and the photoreceptor were rotated so as to trail after the other, wherein the potential of the photoreceptor and the developing bias were adjusted so that a toner image having a weight of 0.6±0.05 mg/cm^2 is formed on the photoreceptor.
(6) The cleaning device of the image forming apparatus included only one cleaning blade having an elasticity of 70%, and a thickness of 2 mm, wherein the blade was set so as to counter the photoreceptor and the angle of the blade is 20˚.
(7) The transfer current was adjusted so that the transfer rate of the toner image is 96±2%.
(8) One thousand (1,000) copies of an original image, which is illustrated in FIG. 7 and which includes a black solid image of 4 cm long and 25 cm wide at the fore-end portion thereof, were produced under the above-mentioned conditions.
(9) A central portion (white portion) of the 1000^{th} copy was visually observed to determine whether the portion has an abnormal image due to defective cleaning.
(10) In addition, the optical densities of the white portion and a reference (i.e., a non-printed sheet of the receiving material) were measured with a densitometer (X-Rite 938 from X-Rite Inc.) to determine the difference between the optical densities.
(11) The cleanability of the toners was graded as follows. O: The optical density difference is not greater than 0.01. (good)
X : The optical density difference is greater than 0.01. (bad)

2. Chargeability of carrier

[0261] Each developer was set in a full color copier, MAGIO COLOR 2800, and a running test in which 30,000 copies of an original image having image area proportion of 50% are produced under an environmental condition of 25 ˚C and 50%RH was performed. In this regard, the color copier was operated in a single color mode. Before and after the running test, part of the developer was sampled to evaluate the charge quantity of the toner (i.e., the chargeability of the carrier) by a blow-off method, namely, to evaluate the difference therebetween. The chargeability of the carrier was graded as follows.

O : The difference between the charge quantities before and after the running test is less than 5 μC/g.
Δ : The difference between the charge quantities before and after the running test is from 5 to 10 μC/g.
X : The difference between the charge quantities before and after the running test is greater than 10 μC/g.

[0262] This evaluation operation was performed at two different toner concentrations of 3% by weight and 12% by weight.

3. Fixability (cold offset temperature (COT) and hot offset temperature (HOT))

[0263] Each developer was set in an image forming apparatus, IMAGIO MF2200 manufactured by Ricoh Co., Ltd., which is modified such that a TEFLON roller is used as the fixing roller. Copies of an image including a solid image of 2.2 cm wide and 7 cm long were produced using a paper TYPE 6200 from Ricoh Co., Ltd., while the fixing temperature was changed at intervals of 5 ˚C to determine the cold offset temperature and the hot offset temperature of the toner. In this regard, the image forming conditions were adjusted to control the weight of the toner image to be 1.0 mg/cm^2.

[0264] The toner images fixed at different fixing temperatures were visually observed to determine whether a cold offset image is observed in the images. The cold offset temperature is defined as the fixing temperature below which a cold offset phenomenon is observed in the resultant fixed images.

[0265] In this regard, the fixing conditions are as follows.

Fixing speed: 120 mm/sec
Fixing pressure : 1.18×10^5 Pa (1.2 Kgf/cm^2) in surface pressure
Fixing nip width: 3 mm.

[0266] The hot offset temperature was determined as follows.

[0267] The images fixed at different fixing temperatures are visually observed to determine whether a hot offset phenomenon occurs.

[0268] The hot offset temperature is defined as a fixing temperature above which a hot offset phenomenon is observed in the fixed images.

[0269] In this regard, the fixing conditions were the same as those in the cold offset temperature determining operation except for the following conditions.

Fixing speed: 50 mm/sec
Fixingpressure: 1.96×10^5 Pa (2.0 Kgf/cm^2) in surface pressure
Fixing nip width: 4.5 mm.

[0270] The evaluation results are shown in Table 2.

Table 2

	Cleanability	Chargeability		Fixability	
		3wt%	12wt%	COT (˚C)	HOT (˚C)
Ex. 1	○	○	○	140	200
Ex. 2	○	○	○	140	200
Ex. 3	○	○	Δ	140	200
Ex. 4	○	○	Δ	140	210
Ex. 5	○	○	○	140	175

(continued)

	Cleanability	Chargeability		Fixability	
		3wt%	12wt%	COT (˚C)	HOT (˚C)
Ex. 6	○	○	○	155	200
Ex. 7	○	○	○	140	195
Comp. Ex. 1	×	Δ	×	140	200
Comp. Ex. 2	○	○	○	140	165
Comp. Ex. 3	×	○	○	140	180
Comp. Ex. 4	×	○	○	140	165

[0271] It is clear from Table 2 that the toner of the present invention has good cleanability without deteriorating the chargeability of the carrier and fixability. Therefore, high quality images can be produced.

Effects of the present invention

[0272] The toner of the present invention has good combination of cleanability and low temperature fixability. In addition, even after long repeated use, the toner hardly deteriorates the chargeability of the carrier used for preparing a two component developer in combination with the toner because of being hardly adhered to the carrier. Therefore, high quality images can be produced over a long period of time. Even when the toner is a near-spherical toner having a small average particle diameter prepared by a granulation method in an aqueous medium, the toner has good cleanability.

[0273] Since the process cartridge uses the toner of the present invention, the process cartridge can also produce high quality images over a long period of time.

[0274] This document claims priority and contains subject matter related to Japanese Patent Application No. 2007-071584, filed on March 19, 2007.

Claims

1. A toner comprising:

a binder resin;
a colorant;
a release agent including a paraffin wax having a melting point of from 60 ˚C to 90 ˚C; and
an inorganic filler including a montmorillonite or modified montmorillonite,

wherein the toner has a circularity of not less than 0. 94, a thermal property such that when the toner is subjected to a differential scanning calorimetric (DSC) analysis, the endothermic quantity calculated from an endothermic peak specific to the paraffin wax is from 3.0 J/g to 6.0 J/g, and a fluidity such that when a cone-shaped rotor having an apex angle of 60 degree and rotated at a speed of 1 rpm is entered into a toner layer by 20 mm in depth at an entering speed of 5 mm /sec, the torque generated by the toner is from 1.4 mNm to 2.0 mNm, wherein the toner layer is prepared by feeding the toner in a cylinder with a diameter of 60 mm and pressing the toner for 60 seconds under a load of 585 g.

2. The toner according to Claim 1, wherein the toner is prepared by a method comprising:

dissolving or dispersing at least a polyester prepolymer having a group including a nitrogen atom, a polyester resin, the colorant, the release agent, and the inorganic filler in an organic solvent to prepare a toner composition liquid;
dispersing the toner composition liquid in an aqueous medium; and
subjecting the polyester prepolymer to at least a reaction selected from the group consisting of crosslinking reactions, molecular chain growth reactions and combinations thereof, and

wherein the toner has a first shape factor SF-1 of from 130 to 160 and a second shape factor of from 110 to 140.

3. The toner according to Claim 1 or 2, wherein the toner has a weight average particle diameter (D4) of from 3 μm to 8 μm, and the ratio (D4/Dn) of the weight average particle diameter (D4) to a number average particle diameter (Dn) of the toner ranges from 1.00 to 1.30.

4. The toner according to any one of Claims 1 to 3, wherein the toner has a glass transition temperature of from 40 ˚C to 60 ˚C.

5. The toner according to any one of Claims 1 to 4, wherein the toner include particles having a particle diameter of not greater than 2 μm in an amount of not greater than 10% by weight based on a total weight of the toner.

6. A process cartridge comprising:

an image bearing member (101) configured to bear an electrostatic image thereon; and
a developing device (104) configured to develop the electrostatic image with a developer including a carrier and the toner according to any one of Claims 1 to 5 to prepare a toner image on the image bearing member,

wherein the process cartridge is detachably attached to an image forming apparatus.

FIG. 1

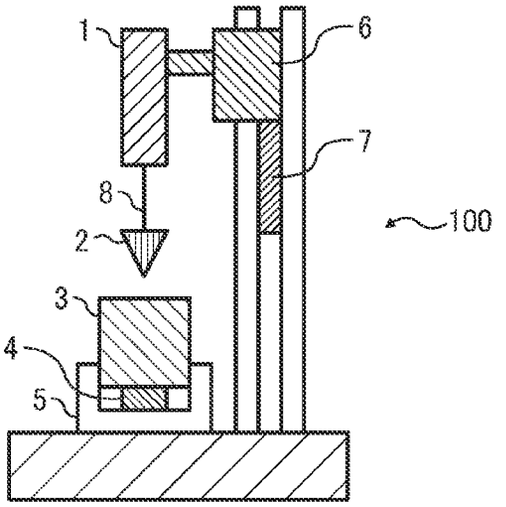


FIG. 2A

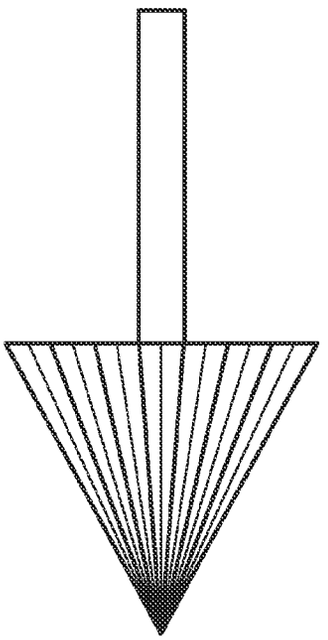


FIG. 2B

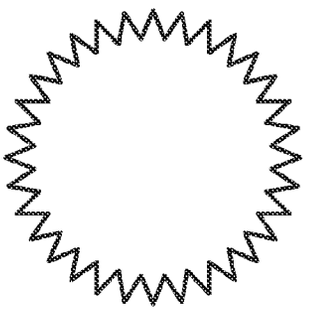


FIG. 3A

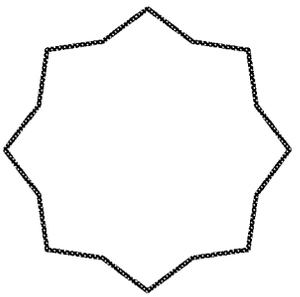


FIG. 3B

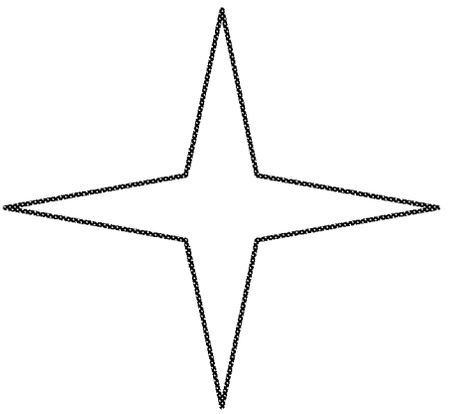


FIG. 3C

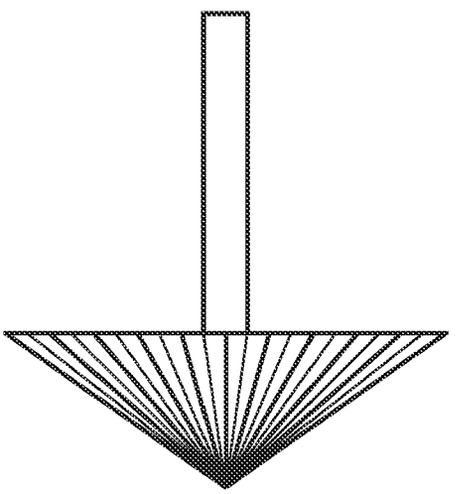


FIG. 4

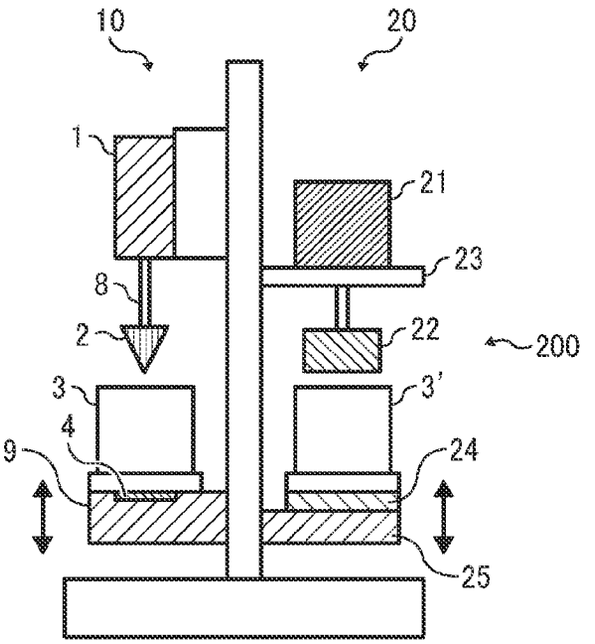


FIG. 5

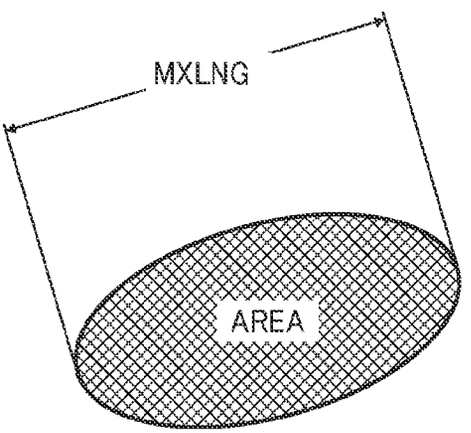


FIG. 6

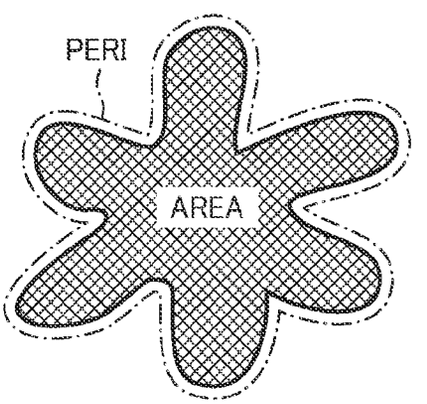


FIG. 7

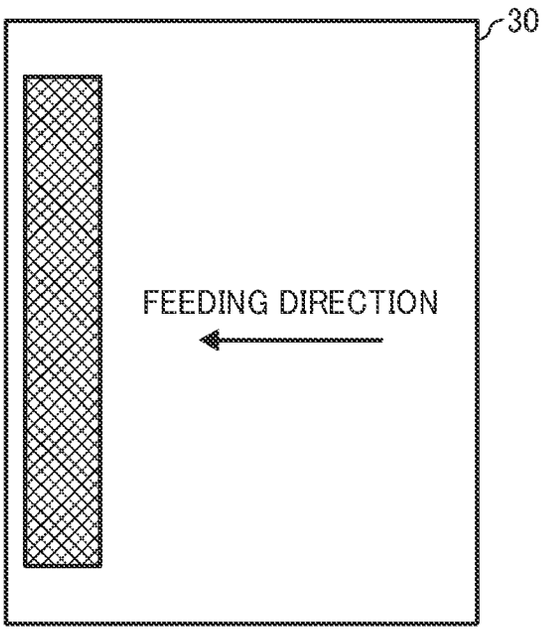
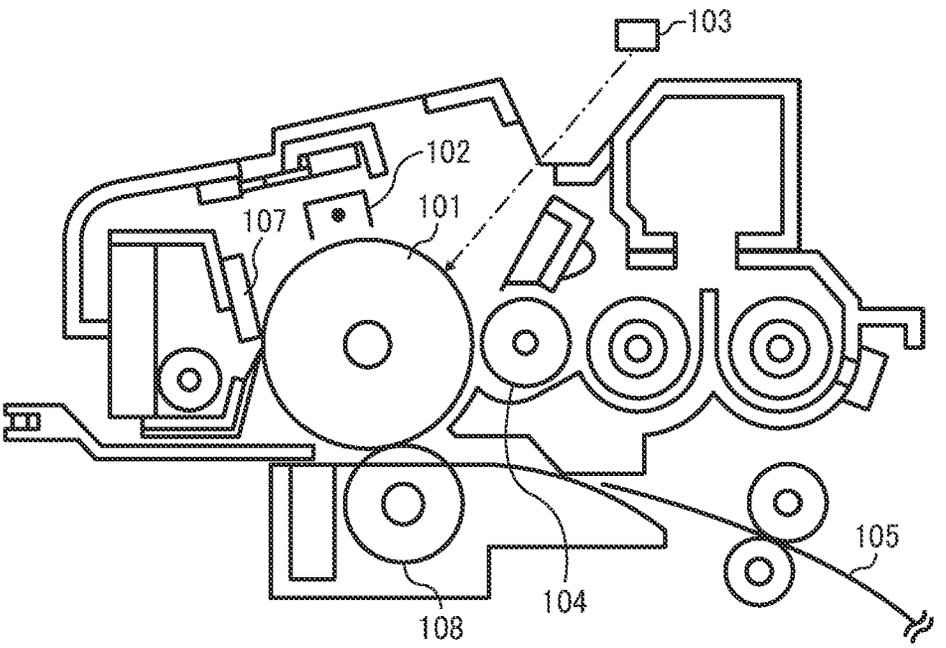


FIG. 8



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Place of search	Date of completion of the search	Examiner
The Hague	24 April 2008	Bolger, Walter

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