(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 3 722 879 A1

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
14.10.2020 Bulletin 2020/42

(51) Int Cl.:
G03G 9/097 ***(2006.01)***

(21) Application number: **20169366.0**

(22) Date of filing: **14.04.2020**

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
KH MA MD TN

(30) Priority: **12.04.2019 JP 2019076426**

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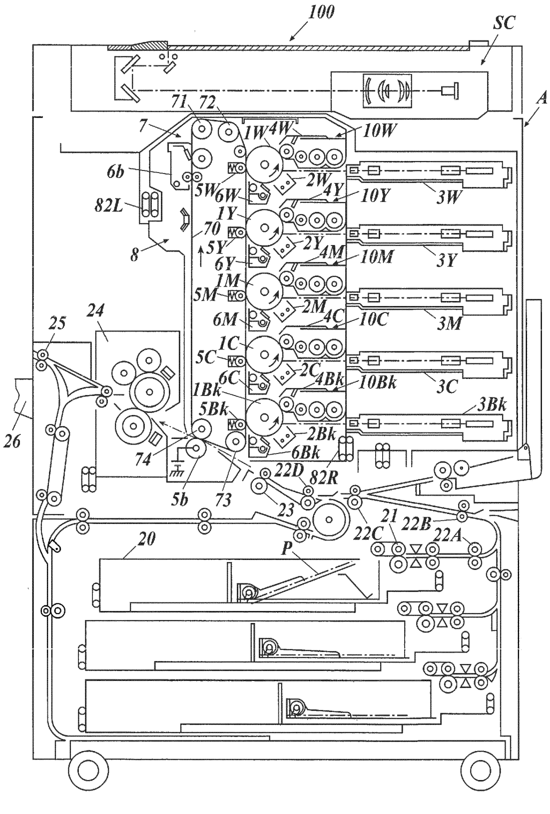
(54) ELECTROSTATIC IMAGE DEVELOPING TONER, PRODUCTION METHOD OF ELECTROSTATIC IMAGE DEVELOPING TONER, AND IMAGE FORMING METHOD

(57) Provided is an electrostatic image developing toner containing toner particles including toner base particles and an external additive, wherein a content of titanium oxide as the external additive is 1 part by mass or less based on 100 parts by mass of the toner base particles; and an amount of metal [A] (CPS) on a surface of a photoreceptor which is measured by X-ray photoelectron spectroscopy after printing 5,000 sheets at 20% coverage on A4 high-quality paper (basis weight: 68 g/m^2) in an environment of 30 °C and 80 %RH and a photoreceptor wear α value [B] satisfy a relationship of the following expression (1) or expression (2), Expression (1): $30,000 \leq [A] \leq 50,000$, Expression (2): $2.50 \leq [B] \leq 5.00$, wherein the photoreceptor wear α value [B] is an amount of wear per 100,000 rotations of the photoreceptor.



Description

BACKGROUND

Technological Field

[0001] The present invention relates to an electrostatic image developing toner, a production method of the electrostatic image developing toner, and an image forming method. In particular, the present invention relates to an electrostatic image developing toner which stably forms a high-quality image for a long period of time while considering environmental safety.

Description of the Related Art

[0002] In recent years, image forming apparatuses have been required to have higher speed, higher image quality, and higher durability. In addition, while the speed of each process for forming an image is accelerated, the life of each component constituting the apparatus is required to be longer from the viewpoint of high definition image and cost reduction. Incidentally, in image formation by an electrophotographic method, an electrostatic latent image is formed on an electrostatic latent image carrier (hereinafter, also referred to as a "photoreceptor"), which is a kind of a constituent member of an image forming apparatus. The formed electrostatic latent image is developed and visualized by a developing toner (hereinafter, also referred to as a "toner"). The toner generally has an external additive for imparting fluidity and controlling charging on the surface of the toner base particles. As an external additive, titanium dioxide (TiO_2), which is a charge control agent, is widely used. However, there is concern about environmental safety of titanium dioxide, and replacement with alternative materials is required.

[0003] In Patent Document 1 (JP-A 2018-155912), a lanthanum-containing titanate compound is used as a substitute material in order to prevent damage to the photoreceptor surface due to titanium dioxide, thereby suppressing image streaks. However, when a lanthanum-containing titanate compound is used, the ability to polish the photoreceptor surface becomes insufficient, and the lubricant tends to remain on the photoreceptor surface. Then, the frictional force on the photoreceptor surface is increased, the cleaning blade is partially drawn in, the toner slips through, and an image defect (raindrop) is likely to occur.

SUMMARY

[0004] The present invention has been made in view of the above problems and circumstances. An object of the present invention is to provide an electrostatic image developing toner, a production method of the electrostatic image developing toner, and an image forming method enabling to maintain the abrasion resistance of the photoreceptor and the cleaning blade, suppress the formation of raindrops due to toner slip-through, form stable high-quality images for a long time, while considering environmental safety.

[0005] The present inventor has found the following in the course of examining the cause of the above-mentioned problem in order to solve the above-mentioned problem. By substantially not containing titanium oxide as an external additive, the amount of metal on the surface of the photoreceptor and the amount of abrasion of the photoreceptor satisfy a specific relational expression, thereby maintaining the abrasion resistance of the photoreceptor and the cleaning blade, and maintaining the abrasion resistance of the raindrop. The present invention enables to provide an electrostatic image developing toner in which generation of the toner is suppressed, a stable high-quality image is formed, and environmental safety is taken into consideration. That is, the above-mentioned object according to the present invention is solved by the following embodiments.

1. To achieve at least one of the above-mentioned objects according to an aspect of the present invention, an electrostatic image developing toner reflecting one aspect of the present invention is a toner containing toner particles comprising toner base particles and an external additive, wherein a content of titanium oxide as the external additive is 1 part by mass or less based on 100 parts by mass of the toner base particles; and an amount of metal [A] (CPS) on a surface of a photoreceptor which is measured by X-ray photoelectron spectroscopy after printing 5,000 sheets at 20% coverage on A4 high-quality paper (basis weight: 68 g/m^2) in an environment of 30 °C and 80 %RH and a photoreceptor wear α value [B] satisfy a relationship of the following expression (1) or expression (2),

$$\text{Expression (1): } 30{,}000 \leq [A] \leq 50{,}000$$

$$\text{Expression (2): } 2.50 \leq [B] \leq 5.00,$$

wherein the photoreceptor wear α value [B] is an amount of wear per 100,000 rotations of the photoreceptor.

2. Another aspect of the present invention is the electrostatic image developing toner described in the embodiment 1, wherein the toner particles contain a fatty acid metal salt.
3. Another aspect of the present invention is the electrostatic image developing toner described in the embodiment 2, wherein the fatty acid metal salt is zinc stearate.
4. Another aspect of the present invention is the electrostatic image developing toner described in the embodiment 3, wherein a content of the zinc stearate is in the range of 0.1 to 1.0 part by mass with respect to 100 parts by mass of the toner base particles.
5. Another aspect of the present invention is the electrostatic image developing toner described in any one of the embodiments 1 to 4, wherein in a measurement of an adhesive strength of the external additive to the toner base particles, when amounts of free external additives of Si, Ti, Ca, Al, Sr, and Zn are represented by [Si], [Ti], [Ca], [Al], [Al], [Sr] and [Zn] (unit: kcps), a relationship of the following expression (3) or expression (4) is satisfied,

$$\text{Expression (3): } 0.5 \leq ([Si] + [Ti] + [Ca] + [Al] + [Sr]) / [Zn]) \leq 2.5,$$

$$\text{Expression (4): } 3.5 \leq ([Si] + [Ti] + [Ca] + [Al] + [Sr]) / [Zn]) \leq 8.0.$$

6. Another aspect of the present invention is the electrostatic image developing toner described in any one of the embodiments 1 to 5, wherein calcium titanate is contained as the external additive.
7. Another aspect of the present invention is the electrostatic image developing toner described in the embodiment 6, wherein a content of the calcium titanate is in the range of 0.1 to 1.0 part by mass with respect to 100 parts by mass of the toner base particles.
8. Another aspect of the present invention is the electrostatic image developing toner described in any one of the embodiments 1 to 7, wherein the toner particles are formed in a split addition of the external additive to the toner base particles.
9. Another aspect of the present invention is a production method of the electrostatic image developing toner described in any one of the embodiments 1 to 8, comprising the step of adding the external additive with a split mixing method to the toner base particles.
10. Another aspect of the present invention is an image forming method using the electrostatic image developing toner described above, wherein a content of titanium oxide as the external additive is 1 part by mass or less based on 100 parts by mass of the toner base particles; and an amount of metal [A] (CPS) on a surface of a photoreceptor which is measured by X-ray photoelectron spectroscopy after printing 5,000 sheets at 20% coverage on A4 high-quality paper (basis weight: 68 g/m^2) in an environment of 30 °C and 80% RH and a photoreceptor wear α value [B] satisfy a relationship of the following expression (1) or expression (2),

$$\text{Expression (1): } 30{,}000 \leq [A] \leq 50{,}000$$

$$\text{Expression (2): } 2.50 \leq [B] \leq 5.00,$$

wherein the photoreceptor wear α value [B] is an amount of wear per 100,000 rotations of the photoreceptor.

BRIEF DESCRIPTION OF THE DRAWINGS

[0006] The advantages and features provided by one or more embodiments of the invention will become more fully understood from the detailed description given hereinbelow and the appended drawings which are given by way of illustration only, and thus are not intended as a definition of the limits of the present invention: wherein, the figure is a schematic cross-sectional view illustrating an example of an electrophotographic image forming apparatus according to the present invention.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0007] Hereinafter, one or more embodiments of the present invention will be described by referring to the drawing. However, the scope of the invention is not limited to the disclosed embodiments. An electrostatic image developing toner of the present invention is a toner containing toner particles comprising toner base particles and an external additive, wherein a content of titanium oxide as the external additive is 1 part by mass or less based on 100 parts by mass of the toner base particles; and an amount of metal [A] (CPS) on a surface of a photoreceptor which is measured by X-ray photoelectron spectroscopy after printing 5,000 sheets at 20% coverage on A4 high-quality paper (basis weight: 68 g/m^2) in an environment of 30 °C and 80 %RH and a photoreceptor wear α value [B] satisfy a relationship of the above-described expression (1) or expression (2). This feature is a technical feature common or corresponding to each of the following embodiments.

[0008] By the above means of the present invention, while maintaining the abrasion resistance of the photoreceptor and the cleaning blade, it is possible to provide an electrostatic image developing toner which enables to suppress the occurrence of raindrops due to toner slippage, to stably form a high-quality image for a long time, and to improve environmental safety. In addition, it is possible to provide a production method of the toner, and an image forming method. The expression mechanism or action mechanism of the effect of the present invention is not clear, but it is presumed as follows.

[0009] In the present invention, the amount of metal [A] (CPS) on the surface of the photoreceptor determined by X-ray photoelectron spectroscopy and the photoreceptor wear α value [B] satisfy the relationship of the above expression (1) or expression (2). This is because when the metal amount [A] (CPS) on the photoreceptor surface is smaller than 30,000, the lubricant uniformly applied to the photoreceptor surface partially disappears, so that the lubricant amount distribution becomes non-uniform, as a result, it is considered that the cleaning blade stick-slips so as to make a large ripple. Then, the toner is drawn in at the stick-slip portion, the toner slips through the cleaning blade and adheres to the photoreceptor, and a linearly attached substance of 1 to 3 mm remains on the photoreceptor. Therefore, it is considered that white spots (raindrops) occur in the image portion. On the other hand, when the metal amount [A] is larger than 50,000, the frictional force on the surface of the photoreceptor increases, and the wear of the cleaning blade increases, so that durability decreases. When the photoreceptor wear α value [B] is less than 2.5, the lubricant on the photoreceptor surface is less likely to be scraped off, so that the lubricant is more likely to adhere to the surface. It is considered that the amount distribution becomes non-uniform caused by local presence of the lubricant, and the cleaning blade sticks and slips in a small wave. Then, the toner is drawn in at the stick-slip portion, the toner slips through the cleaning blade and adheres to the photoreceptor, and a dot or linearly attached substance of 0.1 to 1 mm remains on the photoreceptor. It is considered that white spots (raindrops) occur in the part. On the other hand, when the photoreceptor wear α value [B] is larger than 5.0, the photoreceptor wear increases, and the durability decreases. For the above reasons, by designing the amount of metal [A] (CPS) on the photoreceptor and the photoreceptor wear α value [B] satisfying to the relationship of expression (1) or expression (2), it is assumed that the white point (raindrop) of the image portion can be reduced while maintaining durability. Here, the amount of metal [A] (CPS) is measured by the X-ray photoelectron spectroscopy of the photoreceptor surface after printing 5,000 sheets at a coverage of 20% on A4 high-quality paper (basis weight: 68 g/m^2) in an environment of 30 °C and 80 %RH. And the photoreceptor wear α value [B] is an amount of wear per 100,000 rotations of the photoreceptor.

[0010] As an embodiment of the present invention, it is preferable that the toner particles contain a fatty acid metal salt. In particular, it is preferable that the fatty acid metal salt is zinc stearate, thereby reducing abrasion of the photoreceptor and improving durability. When the content of the zinc stearate is in the range of 0.1 to 1.0 part by mass with respect to 100 parts by mass of the toner base particles, it is preferable in the point that abrasion of the photosensitive member and the cleaning blade is reduced, and durability is improved.

[0011] In a measurement of an adhesive strength of the external additive to the toner base particles, when amounts of free external additives of Si, Ti, Ca, Al, Sr, and Zn are represented by [Si], [Ti], [Ca], [Al], [Al], [Sr] and [Zn] (unit: kcps), it is preferable that a relationship of the above-described expression (3) or expression (4) is satisfied from the viewpoint of suppressing the generation of raindrops, reducing the wear of the photoreceptor, and improving the durability.

[0012] It is preferable to include calcium titanate as the external additive in that wear of the cleaning blade is reduced and durability is improved. When the content of the calcium titanate is in the range of 0.1 to 1.0 part by mass with respect to 100 parts by mass of the toner base particles, it is preferable in the point that wear of the cleaning blade and the photoreceptor is reduced, and durability is improved.

[0013] When the toner particles are formed by adding an external additive to the toner base particles in a divided manner, the adhesion strength to the toner base particles can be controlled for each type of the external additive. It is preferable because the free external additive may be easily adjusted to the range of the above-described expression (3) or expression (4). The term "split addition" means that when the external additive is added to the toner base particles, the whole amount is not added all at once, but is added in portions.

[0014] In a production method of an electrostatic image developing toner of the present invention, an external additive is added to the toner base particles by a split mixing method to produce the electrostatic image developing toner containing the toner particles. Thereby, the adhesion strength to the toner base particles is controlled for each type of the external additive, and the free external additive is easily adjusted within the range of the above-described expression (3) or expression (4). With the two-part addition, the adhesive strength of the external additive added in the second mixture may be reduced. Thereby, the external additive easily rolls on the surface of the base particle, and the fluidity is improved. Furthermore, the contact between the base particle surfaces is suppressed by the spacer effect.

[0015] The image forming method of the present invention is a method using an electrostatic image developing toner including toner particles comprising at least toner base particles and an external additive, wherein a content of titanium oxide as the external additive is 1 part by mass or less based on 100 parts by mass of the toner base particles; and an amount of metal [A] (CPS) on a surface of a photoreceptor which is measured by X-ray photoelectron spectroscopy after printing 5,000 sheets at 20% coverage on A4 high-quality paper (basis weight: 68 g/m^2) in an environment of 30 °C and 80 %RH and a photoreceptor wear α value [B] satisfy a relationship of the above-described expression (1) or expression (2). As a result, while maintaining the abrasion resistance of the photoconductor and the cleaning blade, it is possible to provide an image forming method by which the generation of raindrops due to toner slip-through is suppressed, and high-quality images are formed stably over a long period of time.

[0016] The present invention and the constitution elements thereof, as well as configurations and embodiments, will be detailed in the following. In the present description, when two figures are used to indicate a range of value before and after "to", these figures are included in the range as a lowest limit value and an upper limit value.

[Electrostatic image developing toner]

[0017] An electrostatic image developing toner of the present invention is a toner containing toner particles comprising toner base particles and an external additive, wherein a content of titanium oxide as the external additive is 1 part by mass or less based on 100 parts by mass of the toner base particles; and an amount of metal [A] (CPS) on a surface of a photoreceptor which is measured by X-ray photoelectron spectroscopy after printing 5,000 sheets at 20% coverage on A4 high-quality paper (basis weight: 68 g/m^2) in an environment of 30 °C and 80 %RH and a photoreceptor wear α value [B] satisfy a relationship of the following expression (1) or expression (2),

$$\text{Expression (1): } 30{,}000 \leq [A] \leq 50{,}000$$

$$\text{Expression (2): } 2.50 \leq [B] \leq 5.00,$$

wherein the photoreceptor wear α value [B] is an amount of wear per 100,000 rotations of the photoreceptor.

<Amount of metal on photoreceptor surface>

[0018] In the present invention, an amount of metal [A] on a surface of a photoreceptor refers to an amount of metal contained on a photoreceptor surface detected by X-ray photoelectron spectroscopy when an image is formed using the toner of the present invention, that is, when printing is performed on 5,000 sheets of A4 fine-quality paper (basis weight: 68 g/m^2) at a coverage of 20% in an environment of 30 °C and 80 %RH. In the present invention, it mainly refers to the amount of metal contained in the fatty acid metal salt (lubricant). The amount of metal [A] on the surface of the photoreceptor was determined by quantitative analysis of metal atoms under the following conditions using an X-ray photoelectron spectrometer "K-Alpha" (manufactured by Thermo Fisher Scientific Inc.). The surface element concentration in the range of the outermost surface of the photoreceptor and within 3 nm in the depth direction from the outermost surface were calculated.

(Measurement condition)

[0019]

X-ray:	Al monochromatic X-ray source
Acceleration:	12 kV, 6 mA
Resolution:	50 eV
Beam diameter:	400 μm
Passenergy:	50 eV

(continued)

Step size:	0.1 eV

[0020] The metal amount [A] is in the range of 30,000 to 50,000, and the preferable range is in the range of 30,000 to 40,000 from the viewpoint of suppressing abrasion of the cleaning blade. When the metal amount [A] is less than 30,000, the lubricant uniformly applied to the surface of the photoreceptor partially disappears, so that the lubricant amount distribution becomes non-uniform, and it is considered that the cleaning blade stick-slips so as to make a large ripple. Then, the toner is drawn in the stick-slip portion, and the toner slips through the cleaning blade and adheres to the photoreceptor. It is considered that white spots (raindrops) occur in the image area due to the remaining of the 1 to 3 mm linearly attached substance on the photoreceptor. When the metal amount [A] is larger than 50,000, the frictional force on the surface of the photoreceptor increases, and the wear of the cleaning blade increases.

<Wear amount of photoreceptor>

[0021] When printing 5,000 sheets at a coverage of 20% on A4 high-quality paper (basis weight: $68g/m^2$) in an environment of 30 °C and 80 %RH, 10 random portions of the photoreceptor before and after the durability test (since the film thickness at both ends of the photoreceptor is likely to be non-uniform, at least 3 cm at both ends were avoided) were measured using an eddy current type film thickness measuring device (EDDY560C; HELMUT FISCHER GMBTE Co.), and the average was measured. The value was determined and defined as the thickness of the layer on the photoreceptor. The difference between the thicknesses of the layers before and after the durability test was defined as the amount of wear, and the amount of wear per 100,000 rotations of the photoreceptor was defined as the photoreceptor wear α value [B].

[0022] The above-described wear amount [B] is in the range of 2.50 to 5.00, and a preferable range is in the range of 2.50 to 4.00 in terms of suppressing wear of the photoreceptor. When the wear amount [B] is less than 2.5, the lubricant on the surface of the photoreceptor is hardly scraped off, so that the lubricant easily adheres to the surface, and the partial presence of the lubricant causes uneven distribution of the lubricant amount. And it is considered that the cleaning blade stick-slips so as to undulate. Then, the toner is drawn in the stick-slip portion, and the toner slips through the cleaning blade and adheres to the photoreceptor. It is considered that white spots (raindrops) occur in the image area due to the point-like or line-like deposits of 0.1 to 1 mm remaining on the photoreceptor. On the other hand, when the wear amount [B] is larger than 5.0, the wear of the photoreceptor is increased, and the durability is reduced.

<Toner base particles>

[0023] In the present invention, a "toner" refers to an aggregate of toner particles obtained by adding an external additive to toner base particles. The toner base particles according to the present invention preferably contain components such as a colorant, a release agent, a wax dispersant, and a charge control agent in the binder resin, when needed. Further, an external additive is attached to the surface of the toner base particles according to the present invention.

[0024] The toner base particles according to the present invention preferably contain an amorphous resin and a crystalline resin as the binder resin. Further, the crystalline resin may contain a block polymer.

(Binder resin)

[0025] The crystalline resin is a resin exhibiting crystallinity, and the term "crystallinity" as used in the present invention means that the melting point, that is, the temperature at which the temperature rises, is clear in an endothermic curve obtained by differential scanning calorimetry (DSC). It means having an endothermic peak. The clear endothermic peak means a peak having a half width within 15 °C in an endothermic curve when the temperature is increased at a rate of 10 °C/min. Further, the amorphous resin is a resin exhibiting the amorphous property, and the term "having the amorphous property" in the present invention means that the above-mentioned endothermic curve does not have a clear endothermic peak at the melting point, that is, when the temperature is raised.

[0026] From the viewpoint of achieving both heat resistance and low-temperature fixability, the toner base particles preferably have a matrix-domain structure in which an amorphous resin having excellent heat resistance is used as a matrix, and a crystalline resin that imparts low-temperature fixability is dispersed in the matrix as domains.

(Crystalline resin)

[0027] The binder resin according to the present invention preferably contains a crystalline resin from the viewpoint of improving low-temperature fixability. The content of the crystalline resin in the toner base particles is preferably in the range of 1 to 20% by mass, more preferably in the range of 5 to 20% by mass, and still more preferably in the range of 7 to 15% by mass. When the content is 1% by mass or more, the effect of low-temperature fixability may be effectively exhibited. Further, by setting the content of the crystalline resin in the toner base particles to 20% by mass or less, the interface between the crystalline resin and the amorphous resin may be reduced. Therefore, the area of the interface portion which is likely to be a starting point of the toner base particles is reduced, and the toner base particles can be hardly broken. Therefore, the toner hardly scatters.

(Crystalline polyester resin)

[0028] From the viewpoint of obtaining better low-temperature fixability, the toner base particles preferably contain a crystalline polyester resin as the crystalline resin.

[0029] The crystalline polyester resin is a polyester resin exhibiting crystallinity among known polyester resins obtained by a polycondensation reaction between a divalent or higher carboxylic acid (polyhydric carboxylic acid) component and a divalent or higher valent alcohol (polyhydric alcohol) component.

[0030] The method for synthesizing the crystalline polyester resin is not particularly limited. A crystalline polyester resin may be formed by polymerizing (esterifying) the polyhydric carboxylic acid component and the polyhydric alcohol component using an esterification catalyst.

[0031] The polycarboxylic acid component for forming the crystalline polyester resin is a compound containing two or more carboxy groups per molecule. Specific examples thereof include: saturated aliphatic dicarboxylic acids such as oxalic acid, malonic acid, succinic acid, adipic acid, sebacic acid, azelaic acid, n-dodecylsuccinic acid, 1,10-decanedicarboxylic acid (dodecandioic acid), 1,12-dodecanedicarboxylic acid (tetradecandioic acid); alicyclic dicarboxylic acids such as cyclohexanedicarboxylic acid; aromatic dicarboxylic acids such as phthalic acid, isophthalic acid, and terephthalic acid; polycarboxylic acids of trivalent or higher such as trimellitic acid and pyromellitic acid; and anhydrides or alkyl esters having 1 to 3 carbon atoms of these carboxylic acid compounds. These may be used alone or may be used in combination of two or more.

[0032] The polyhydric alcohol component for forming the crystalline polyester resin is a compound having two or more hydroxy groups per molecule. Specific examples thereof include: aliphatic diols such as 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, neopentyl glycol, and 1,4-butenediol; and polyhydric alcohols of trihydric or higher alcohols such as glycerin, pentaerythritol, trimethylolpropane, and sorbitol. These may be used alone or may be used in combination of two or more.

[0033] Examples of a usable catalyst for synthesizing a crystalline polyester resin of the present invention are: alkali metal compounds made of sodium and lithium; alkali earth metal compounds made of magnesium and calcium; metal compounds made of metals such as aluminum, zinc, manganese, antimony, titanium, tin, zirconium, and germanium; phosphorous acid compounds, phosphoric acid compounds, and amine compounds.

[0034] The polymerization temperature is not particularly limited, but it is preferably in the range of 150 to 250 °C. The polymerization time is not particularly limited, but it is preferably in the range of 0.5 to 10 hours. During the polymerization, the pressure in the reaction system may be reduced when needed.

[0035] The melting point (Tm) of the crystalline resin such as the crystalline polyester resin is preferably in the range of 65 to 85 °C from the viewpoint of achieving excellent low-temperature fixability, heat resistance and hot offset resistance. The temperature is more preferably in the range of 70 to 80 °C.

[0036] The melting point (Tm) is the temperature at the peak of the endothermic peak and it can be measured by DSC. Specific measurement is done as follows. First, a measuring sample is sealed in an aluminum pan (KIT NO. B0143013) and it is set to a sample holder of a thermal analysis instrument "Diamond DSC" (PerkinElmer Inc.) The temperature is changed in the order of heating-cooling-heating. In the first heating step, the temperature is increased from room temperature (25 °C) to 150 °C at a heating rate of 10 °C/min, then the temperature is kept at 150 °C for 5 minutes. In the cooling step, the temperature is decreased from 150 °C to 0 °C at a cooling rate of 10 °C/min. Then the temperature is kept at 0 °C for 5 minutes. The peak top temperature of the endothermic peak in the endothermic curve obtained in the second heating step is taken as a melting point (Tm).

[0037] Further, the absolute value of the difference between the number of carbon atoms of the polyhydric alcohol component and the number of carbon atoms of the polyvalent carboxylic acid component constituting the crystalline polyester resin is preferably 3 or more.

[0038] In addition, the content of the crystalline polyester resin in the crystalline resin is preferably in the range of 1 to 10% by mass.

(Amorphous resin)

[0039] As the amorphous resin, for example, a vinyl resin or an amorphous polyester resin may be used. A vinyl resin is a polymer of a vinyl monomer. Specific examples of the vinyl resin include a styrene resin, an acrylic resin, and a styrene-acryl resin.

[0040] From the viewpoint of obtaining excellent heat-resistant storage properties, the toner base particles preferably contain a styrene-acrylic resin as a binder resin, and the content of the styrene-acrylic resin in the toner base particles is preferably 5% by mass or more. From the viewpoint of achieving both heat storage stability and low-temperature fixability, the content of the styrene-acrylic resin in the toner base particles is preferably 80% by mass or less.

[0041] The vinyl monomer is a polymerizable monomer having a vinyl group, and one type may be used alone or two or more types may be used in combination. The following monomers are examples of vinyl monomers. Among them, a polymer having a crosslinked structure may be obtained by using a polyfunctional vinyl monomer. The styrene-acrylic resin may be a copolymer obtained by combining a styrene monomer and a (meth)acrylic acid monomer with another vinyl monomer.

(1) Styrene monomers

[0042] Styrene, o-methylstyrene, m-methylstyrene, p-methylstyrene, α-methylstyrene, p-phenylstyrene, p-ethylstyrene, 2,4-dimethylstyrene, p-tert-butylstyrene, p-n-hexylstyrene, p-n-octylstyrene, p-n-nonylstyrene, p-n-decylstyrene, and p-n-dodecylstyrene; and derivatives of these monomers having a styrene structure.

(2) (Meth)acrylic acid monomers

[0043] (Meth)acrylic acid, methyl (meth)acrylate, ethyl (meth)acrylate, n-butyl (meth)acrylate, isopropyl (meth)acrylate, isobutyl (meth)acrylate, t-butyl (meth)acrylate, n-octyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, stearyl (meth)acrylate, lauryl (meth)acrylate, phenyl (meth)acrylate, diethylaminoethyl (meth)acrylate, dimethylaminoethyl (meth)acrylate; and derivatives of these monomers having a (meth)acrylic acid structure.

(3) Vinyl esters

[0044] Vinyl propionate, vinyl acetate, and vinyl benzoate.

(4) Vinyl ethers

[0045] Vinyl methyl ether, and vinyl ethyl ether.

(5) Vinyl ketones

[0046] Vinyl methyl ketone, vinyl ethyl ketone, and vinyl hexyl ketone.

(6) N-vinyl compounds

[0047] N-vinylcarbazole, N-vinylindole, and N-vinylpyrrolidone.

(7) Others

[0048] Vinyl compounds such as vinyl naphthalene and vinyl pyridine, acrylic acid or methacrylic acid derivatives such as acrylonitrile, methacrylonitrile and acrylamide.

(8) Polyfunctional vinyls

[0049] Divinylbenzene, ethylene glycol dimethacrylate, ethylene glycol diacrylate, diethylene glycol dimethacrylate, diethylene glycol diacrylate, triethylene glycol dimethacrylate, triethylene glycol diacrylate, neopentyl glycol dimethacrylate, and neopentyl glycol diacrylate.

[0050] Among them, a vinyl monomer having an acid group is preferable because the vinyl resins are easily ion-crosslinked, and by adjusting the content of the acid group in the vinyl resin, the degree of ionic cross-linking is easily controlled. The acid group refers to an ionic dissociating group such as a carboxy group, a sulfonic group, and a phosphate group. For example, examples of the vinyl monomer having a carboxy group include acrylic acid, methacrylic acid, maleic acid, itaconic acid, cinnamic acid, fumaric acid, monoalkyl maleate, and monoalkyl itaconate. Examples of the vinyl monomer having a sulfonic acid group include styrenesulfonic acid, allylsulfosuccinic acid, and 2-acrylamido-2-methylpropanesulfonic acid. Examples of the vinyl monomer having a phosphate group include acid phosphooxyethyl methacrylate.

[0051] The glass transition point (Tg) of the vinyl resin is preferably in the range of 20 to 70 °C from the viewpoint of achieving both low-temperature fixability and heat-resistant storage stability.

[0052] From the viewpoint of obtaining excellent heat resistance, the content of the vinyl resin in the toner base particles is preferably 5% by mass or more, more preferably 20 to 60% by mass, and still more preferably 35 to 60% by mass.

(Amorphous polyester resin)

[0053] An amorphous polyester resin refers to a resin exhibiting amorphousness among polyester resins obtained by a polymerization reaction between a polyvalent carboxylic acid component and a polyhydric alcohol component. An amorphous polyester resin may be synthesized by polymerizing a polyhydric carboxylic acid component and a polyhydric alcohol component using an esterification catalyst in the same manner as the above-mentioned crystalline polyester resin.

[0054] Examples of the polyvalent carboxylic acid component that may be used for the synthesis of an amorphous polyester resin include: phthalic acid, isophthalic acid, terephthalic acid, trimellitic acid, naphthalene-2,6-dicarboxylic acid, malonic acid, mesaconic acid, dimethyl isophthalate, fumaric acid, dodecenylsuccinic acid, and 1,10-decanedicarboxylic acid.

[0055] Examples of the polyhydric alcohol component that may be used for the synthesis of an amorphous polyester resin include divalent or trivalent alcohols such as ethylene glycol, propylene glycol, 1,4-butanediol, 2,3-butanediol, diethylene glycol, triethylene glycol, 1,5-pentanediol, 1,6-hexanediol, neopentyl glycol, 1,4-cyclohexanedimethanol, dipropylene glycol, polyethylene glycol, polypropylene glycol, ethylene oxide adduct of bisphenol A (BPA-EO), propylene oxide adduct of bisphenol A (BPA-PO), glycerin, sorbitol, 1,4-sorbitan, and trimethylol propane. Among these, an ethylene oxide adduct of bisphenol A and a propylene oxide adduct of bisphenol A are preferred.

(Colorant)

[0056] The number average primary particle diameter of the colorant varies depending on the type, but it is preferably about 10 to 200 nm. The content ratio of the colorant in the toner is preferably in the range of 1 to 30% by mass, more preferably 2 to 20% by mass, based on the total mass of the binder resin in the toner.

(Release agent)

[0057] The release agent is not particularly limited, and various known waxes can be used. Examples of the usable release agent include: polyolefin waxes such as polyethylene wax and polypropylene wax; branched hydrocarbon waxes such as microcrystalline wax; long-chain hydrocarbon waxes such as paraffin wax and SASOL wax; dialkyl ketone waxes such as distearyl ketone; ester waxes such as carnauba wax, montan wax, behenyl behenate, trimethylolpropane tribehenate, pentaerythritol tetrabehenate, pentaerythritol diacetate dibehenate, glycerol tribehenate, 1,18-octadecanediol distearate, tristearyl trimellitate, and distearyl maleate; and amide waxes such as ethylenediaminebehenylamide and trimellitic tristearylamide.

[0058] The use of a hydrocarbon wax as the release agent improves the dispersibility of the wax in the binder resin, and prevents the toner from being broken at the interface between the resin and the wax due to external stress. This is preferable because the effect of suppressing image white spots can be obtained.

[0059] The content of the release agent in the toner base particles is preferably in the range of 3 to 15 parts by mass from the viewpoint of obtaining sufficient fixing and separating properties.

(Charge control agent)

[0060] A variety of known compounds may be used as a charge control agent. Examples thereof include: nigrosine dyes, metal salts of naphthenic acid or higher fatty acids, alkoxylated amines, quaternary ammonium salts, azo metal complexes, and salicylic acid metal salts. By adding a charge control agent, a toner having excellent charging characteristics may be obtained. The content of the charge control agent is preferably in the range of 0.1 to 5.0% by mass based on the total amount of the binder resin.

(Core-shell structure)

[0061] Although the toner base particles described above may be used as the toner as they are, the toner base particles may be core particles, and a core-shell structure may be formed by providing a shell layer covering the surface of the core particles. Here, the core-shell structure is not limited to a structure in which the shell layer completely covers the core particle. It includes a structure in which a part of the core particle is exposed. The cross-sectional structure of the core-shell structure may be observed and confirmed with a known method such as a transmission electron microscope

(TEM) or a scanning probe microscope (SPM).

[0062] In the case of the core-shell structure, the core particle and the shell layer each may have different glass transition point, melting point, and hardness. As a result, it is possible to make a toner design corresponding to the purpose. For example, a shell layer may be formed by aggregated and fused a resin having a high glass transition point (Tg) on the surface of a core particle containing a binder resin, a coloring agent and a releasing agent, and having a low glass transition point (Tg).

[0063] The glass transition point (Tg) of the toner is preferably in the range of 40 to 60 °C, more preferably in the range of 45 to 55 °C. By being in this range, sufficient low-temperature fixability and heat-resistant storage stability can be reliably obtained. Further, when the glass transition point of the toner is in the above range, the heat resistance (thermal strength) of the toner is maintained, and as a result, sufficient heat storage stability and hot offset resistance are reliably obtained.

(Fatty acid metal salt)

[0064] It is preferable that the toner particles according to the present invention contain a fatty acid metal salt in terms of reducing abrasion of the photoreceptor and improving durability. The fatty acid metal salt is preferably contained as a lubricant. As the fatty acid metal salt, a metal salt selected from zinc, calcium, magnesium, aluminum and lithium is preferable. Among them, a metal salt of zinc, lithium or calcium is preferred from the viewpoint of enhancing lubricity. As the fatty acid of the fatty acid metal salt, a higher fatty acid having 12 to 22 carbon atoms is preferable. When a fatty acid having 12 or more carbon atoms is used, generation of a free fatty acid metal salt may be suppressed, and when a fatty acid having 22 or less carbon atoms is used, the melting point of the fatty acid metal salt does not become too high, and good fixing property is obtained. Stearic acid is particularly preferred as the fatty acid. Therefore, specific examples thereof includes higher fatty acid metal salts such as: zinc, aluminum, copper, magnesium, or calcium stearate; zinc, manganese, iron, copper, or magnesium oleate; zinc, copper, magnesium, or calcium palmitate; zinc or calcium linolenate; and zinc or calcium ricinoleate. In particular, zinc stearate is preferred in that it reduces wear on the photoreceptor and improves durability.

[0065] When zinc stearate is used as the fatty acid metal salt, the content of the zinc stearate in the toner particles is preferably in the range of 0.1 to 1.0 part by mass based on 100 parts by mass of the toner base particles. When the amount is 0.1 part by mass or more, the wear of the photoreceptor is reduced and the durability is improved. When the amount is 1.0 part by mass or less, the wear of the cleaning blade is reduced and the durability is improved.

<External additive>

[0066] The toner particles according to the present invention contain an external additive.

[0067] In the present invention, the content of titanium oxide as an external additive is 1 part by mass or less based on 100 parts by mass of the toner base particles. That is, as long as the requirements of the present invention are satisfied and the effects of the present invention are not impaired, titanium oxide particles may be contained as an external additive. Note that it is preferable not to include an amount that affects the environment, and particularly preferable not to include titanium oxide at all.

<Amount of free external additive>

[0068] In the measurement of the adhesion strength of the external additive to the toner base particles according to the present invention, it is preferable that the amounts of the free external additives of Si, Ti, Ca, Al, Sr, and Zn each represented by [Si], [Ti], [Ca], and [Al], [Sr], [Zn] (unit: kcps) satisfy a relationship of the following expression (3) or expression (4) from the viewpoint of suppressing raindrop generation, reducing wear of the photoreceptor, and improving durability.

$$\text{Expression (3): } 0.5 \leq ([\mathrm{Si}] + [\mathrm{Ti}] + [\mathrm{Ca}] + [\mathrm{Al}] + [\mathrm{Sr}]) / [\mathrm{Zn}]) \leq 2.5$$

$$\text{Expression (4): } 3.5 \leq ([\mathrm{Si}] + [\mathrm{Ti}] + [\mathrm{Ca}] + [\mathrm{Al}] + [\mathrm{Sr}]) / [\mathrm{Zn}]) \leq 8.0$$

[0069] When the value of ([Si] + [Ti] + [Ca] + [Al] + [Sr]) / [Zn]) is more than 2.5, raindrops occur. Wear increases and durability decreases. In terms of suppressing the wear of the cleaning blade, a preferable range is 1.0 ≤ ([Si] + [Ti] + [Ca] + [Al] + [Sr]) / [Zn]) ≤2.5. When the value of ([Si] + [Ti] + [Ca] + [Al] + [Sr]) / [Zn]) is smaller than 3.5, a raindrop occurs. When it is larger than 8.00, the abrasion of the photoreceptor is increased and the durability is reduced. From the viewpoint of suppressing abrasion of the photoreceptor, a preferable range is $3.5 \leq ([Si] + [Ti] + [Ca] + [Al] + [Sr]) / [Zn]) \leq 7.5$.

[0070] The amount of the free external additive are calculated as follows. 3 g of each toner is wetted with 35 g of a 0.2% aqueous solution of polyoxyethyl phenyl ether. Using an ultrasonic homogenizer US-1200T (manufactured by Nippon Seiki Co., Ltd.: specification frequency 15 kHz), the ultrasonic energy is adjusted so that the value of the ammeter indicating the vibration indication value attached to the main unit indicates 60 μA (50 W), then impresses a voltage for 2 minutes. Thereafter, the toner cake layer is washed with 60 g of pure water by suction filtration, the toner is reslurried in 60 g of pure water, and suction filtration is performed again. The toner is taken out and dried overnight in a thermostat at 50 °C to obtain a deteriorated toner. Using a fluorescent X-ray analyzer "XRF-1700" (manufactured by Shimadzu Corporation), the Net intensity of the metal amount is measured. As a specific method of measuring the Net strength, 2 g of the toner is pressed under a load of 15 t for 10 seconds, pelletized to a size of 40 mmφ, and measured by qualitative and quantitative analysis (see the following measurement conditions). The $K\alpha$ peak angles of the Si element, Ti element, Ca element, Al element, Sr element, and Zn element to be measured are determined from the 2θ table and used. The difference in Net strength calculated from the Net strength (unit: kcps) of the Si element, Ti element, Ca element, Al element, Sr element, and Zn element before and after the deterioration of the toner is defined as the liberation amount of the external additive in the sample toner. Then, the value of the ratio of the total amount ([Si] + [Ti] + [Ca] + [Al] + [Sr]) of the free amount of other external additives to the free amount [Zn] of zinc stearate, that is, ([Si] + [Ti] + [Ca] + [Al] + [Sr]) / [Zn] is calculated.

[Measurement conditions]

[0071]

Slit: Standard
Attenuator: None
Spectral crystal (Na = TAP)
Detector (Na = FPC)

[0072] The external additive according to the present invention preferably contains aluminum oxide particles. By containing the aluminum oxide particles, since the hardness of the aluminum oxide is high, so that the friction between the cleaning blade and the photoreceptor makes it easy for the aluminum oxide particles to be buried in the toner, and the fluidity of the toner particles decreases. For this reason, the toner particles easily stay between the cleaning blade and the photoreceptor, and the toner layer densely packed with the toner particles enhances the effect of damping small-diameter toner and external additives, thereby suppressing the occurrence of image white spots.

[0073] Further, the primary particle size of the aluminum oxide particles is preferably in the range of 10 to 80 nm, which is a size that may be appropriately buried in the toner particles in order to exhibit the above-described effect of image white spots.

[0074] The toner particles according to the present invention may contain other external additives. Other external additives include, for example, silica particles, and inorganic titanate compound particles such as strontium titanate, zinc titanate, and calcium titanate. Further, inorganic stearic acid compound particles such as aluminum stearate particles and zinc stearate particles used as the lubricant are also included. These may be used alone or in combination of two or more. In particular, it is preferable to contain calcium titanate particles as an external additive in terms of reducing abrasion of the cleaning blade and improving durability. The inorganic particles used as the external additive are preferably subjected to a gloss treatment with a silane coupling agent, a titanium coupling agent, a higher fatty acid, or silicone oil from the viewpoint of improving heat resistance storage stability and environmental stability.

[0075] The added amount of the external additive (when a plurality of external additives are used, the total added amount) is preferably in the range of 0.05 to 5 parts by mass with respect to 100 parts by mass of the toner. More preferably, the amount is in the range of 0.1 to 3 parts by mass. When calcium titanate particles are used as the external additive, the content of calcium titanate is preferably in the range of 0.1 to 1.0 part by mass based on 100 parts by mass of the toner base particles. When the amount is 0.1 parts by mass or more, the abrasion of the cleaning blade is small and the durability is improved. When the amount is 1.0 parts by mass or less, the abrasion of the photoreceptor is small and the durability is improved.

[Production method of electrostatic image developing toner]

[0076] In the producing method of an electrostatic image developing toner of the present invention, an external additive is added to the toner base particles by a split mixing method to produce an electrostatic image developing toner containing the toner particles. That is, in order for the metal amount [A] on the photoreceptor surface and the photoreceptor wear α value [B] to satisfy the relationship of the above-described expression (1) or expression (2), an external additive is added by a split mixing method in the external additive addition step. Examples of the producing method for an electrostatic image developing toner of the present invention include a suspension polymerization method, an emulsion aggregation method, and other known methods. From the viewpoint of production cost and production stability, it is preferable to use an emulsion aggregation method that can easily reduce the particle size of the toner base particles.

[0077] The method for producing toner base particles by the emulsification aggregation method comprises mixing an aqueous dispersion of binder resin particles and an aqueous dispersion of colorant particles, and aggregating the binder resin particles and the colorant particles to form toner base particles.

[0078] Here, the aqueous dispersion refers to one in which particles are dispersed in an aqueous medium, and the aqueous medium refers to one in which 50% by mass or more of the main component in the aqueous medium is water. Components other than water in the aqueous medium include organic solvents that dissolve in water. Examples thereof are: methanol, ethanol, isopropanol, butanol, acetone, methyl ethyl ketone, and tetrahydrofuran. Among them, alcoholic organic solvents such as methanol, ethanol, isopropanol and butanol, which are organic solvents that do not dissolve the resin, are preferred.

[0079] Hereinafter, an example of steps of a method for producing a toner by an emulsion aggregation method will be described.

<Step (1)>

[0080] In the step (1), dispersions of binder resin particles such as a crystalline resin and an amorphous resin are respectively prepared.

[0081] For example, when a crystalline polyester resin is used as a crystalline resin, a crystalline polyester resin is synthesized, then, an oil phase liquid is prepared by dissolving or dispersing it in an organic solvent, and this oil phase liquid is subjected to phase inversion emulsification. The polyester resin particles are dispersed in an aqueous medium. After controlling the particle size of the oil droplets to a desired particle size, the aqueous solvent of the polyester resin may be obtained by removing the organic solvent.

[0082] As the organic solvent used for the oil phase liquid, those having a low boiling point and low solubility in water are preferred from the viewpoint of easy removal treatment after the formation of oil droplets. Specific examples include methyl acetate, ethyl acetate, methyl ethyl ketone, methyl isobutyl ketone, toluene, and xylene. These may be used alone or in combination of two or more. The amount of the organic solvent used is usually in the range of 1 to 300 parts by mass with respect to 100 parts by mass of the crystalline polyester resin. Emulsification and dispersion of the oil phase liquid may be performed using mechanical energy.

[0083] The amount of the aqueous medium to be used is preferably in the range of 50 to 2,000 parts by mass, more preferably in the range of 100 to 1,000 parts by mass, per 100 parts by mass of the oil phase liquid. A surfactant may be added to the aqueous medium for the purpose of improving the dispersion stability of oil droplets.

[0084] The average particle size of the crystalline polyester resin particles is preferably in the range of 100 to 400 nm in terms of volume-based median diameter (D_{50}). The volume-based median diameter (D_{50}) of the crystalline polyester resin particles may be measured using Microtrac UPA-150 (manufactured by Nikkiso Co., Ltd.).

[0085] When a vinyl resin is used as the binder resin, an aqueous dispersion of vinyl resin particles can be prepared by a mini-emulsion polymerization method. Specifically, a vinyl monomer and a water-soluble radical polymerization initiator are added to an aqueous medium containing a surfactant, and mechanical energy is applied to form droplets. The polymerization reaction proceeds in the droplets due to radicals from the radical polymerization initiator. Note that an oil-soluble polymerization initiator may be contained in the droplet.

[0086] The vinyl resin particles may have a multilayer structure of two or more layers in which the composition of each layer is different. A dispersion of vinyl resin particles having a multilayer structure may be obtained by a multi-stage polymerization reaction. For example, a dispersion of a vinyl resin having a two-layer structure is prepared by polymerizing a vinyl monomer (first-stage polymerization) to prepare a dispersion of vinyl resin particles, and further adding a polymerization initiator and a vinyl monomer. Then, polymerization (second stage polymerization) is performed to obtain a vinyl resin having a two-layer structure.

(Surfactant)

[0087] Examples of the surfactant to be used are: cationic surfactants such as dodecyl ammonium bromide and dodecyl trimethyl ammonium bromide; anionic surfactants such as dodecyl polyoxyethylene ether, hexadecyl polyoxyethylene ether, norylphenyl polyoxyethylene ether, lauryl polyoxyethylene ether, and sorbitan monooleate polyoxyethylene ether; and nonionic surfactants such as sodium stearate, sodium laurate, sodium lauryl sulfate, sodium dodecylbenzenesulfonate, and sodium dodecyl sulfate.

(Polymerization initiator)

[0088] As the polymerization initiator, conventionally known various ones may be used. As the polymerization initiator, persulfates (potassium persulfate, ammonium persulfate, etc.) are preferably used. However, azo compounds such as 4,4'-azobis(4-cyanovaleric acid) and salts thereof, 2,2'-azobis(2-amidinopropane) salts, peroxide compounds, and azobisisobutyronitrile may also be suitable used.

(Chain transfer agent)

[0089] For the purpose of adjusting the molecular weight of the vinyl resin, a generally used chain transfer agent may be added to the aqueous medium. The chain transfer agent is not particularly limited, and examples thereof include: mercaptans such as 2-chloroethanol, octylmercaptan, dodecylmercaptan, t-dodecylmercaptan, n-octyl-3-mercaptopropionate, and styrene dimers.

[0090] When producing toner base particles containing additives such as a release agent and a charge control agent, the additive may be introduced into the toner base particles by dissolving or dispersing the additive in the vinyl monomer solution in advance. Thus, it is preferable to disperse the additive in advance with the vinyl resin particles, but it is possible to prepare as follows. A dispersion liquid of the additive particles is prepared separately from the vinyl resin, mixed it with another dispersion liquid such as the polyester resin particles, and is introduced into the toner base particles by aggregating the additive particles together with the polyester resin particles.

[0091] The average particle size of the vinyl resin particles in the dispersion liquid is preferably in the range of 100 to 400 nm in terms of volume-based median diameter (D_{50}). The volume-based median diameter (D_{50}) of the vinyl resin particles may be measured using Microtrac UPA-150 (manufactured by Nikkiso Co., Ltd.).

<Step (2)>

[0092] In the step (2), the colorant is dispersed in the form of particles in an aqueous medium to prepare an aqueous dispersion of colorant particles.

[0093] The aqueous dispersion of the colorant particles may be obtained by dispersing the colorant in an aqueous medium in which a surfactant is added at a critical micelle concentration (CMC) or higher. Dispersion of the colorant may be performed using mechanical energy, and the disperser to be used is not particularly limited. Preferable examples include an ultrasonic dispersing machine, a mechanical homogenizer, a pressure dispersing machine such as Manton Gaulin and a pressure type homogenizer, and a medium dispersing machine such as a sand grinder, a Getzmann mill and a diamond fine mill.

[0094] The colorant particles in the aqueous dispersion preferably have a volume-based median diameter (D_{50}) in the range of 10 to 300 nm, more preferably in the range of 100 to 200 nm, and still more preferably in the range of 100 to 150 nm. The volume-based median diameter (D_{50}) of the colorant particles may be measured using an electrophoretic light scattering photometer ELS-800 (manufactured by Otsuka Electronics Co., Ltd.).

<Step (3)>

[0095] In the step (3), in the presence of an aggregating agent (or may be called as a flocculant), binder resin particles such as vinyl resin particles and polyester resin particles, colorant particles, and particles of other toner components are aggregated to form toner base particles. Specifically, a flocculant having a critical aggregating concentration or higher is added to a system in which an aqueous medium and an aqueous dispersion of each particle are mixed, and aggregation is performed by adjusting the temperature to a temperature higher than the glass transition point (Tg) of the vinyl resin.

(Flocculant)

[0096] The flocculant used in this step is not limited in particular, but it is preferably selected from metal salts of alkali metal salts and alkali earth metal salts. Such metal salts include, for example, monovalent metal salts such as salts of sodium, potassium and lithium; divalent metal salts of calcium, magnesium, manganese and copper; and trivalent metal salts of iron and aluminum. Specific examples of such metal salts include sodium chloride, potassium chloride, lithium chloride, calcium chloride, magnesium chloride, zinc chloride, copper sulfate, magnesium sulfate, and manganese sulfate. Among them, divalent metal salts are particularly preferred since the aggregation is caused by a smaller amount. These flocculants may be used alone, or they may be used in combination of two or more kinds.

<Step (4)>

[0097] In the step (4), the toner base particles formed by the step (3) are aged to change the shape of the toner particles into a required shape. This step (4) is done according to necessity. Specifically, the dispersion liquid of the toner base particles formed by the step (3) is heated with stirring. The heating temperature, stirring speed and heating time are controlled so that the average circularity of the aggregated toner based particles reaches a desired level.

<Step (4B)>

[0098] In the step (4B), the toner base particles obtained in the step (3) or the step (4) are used as core particles. A shell layer is formed on the core particle so that at least a part of the surface of the core particle is covered. The step (4B) is done only when toner base particles having a core-shell structure are produced.

[0099] When toner base particles having a core-shell structure are produced, they may be produced by the following method. A resin that constitutes a shell layer is dispersed in an aqueous medium to prepare a dispersion liquid of resin particles for a shell layer. This dispersion liquid for a shell layer is added to the dispersion liquid of the toner base particles obtained in the step (4) or the step (5). The resin particles for a shell layer are aggregated and fused on the surface of the toner base particles. By this, it may be obtained a dispersion liquid of toner base particles having a core-shell structure. For the purpose of more strongly aggregating and fusing the resin particles for a shell layer on the core particles, a heating treatment may be done after the shell forming step. The heating treatment may be done until the moment of obtaining toner base particles reaching a required circularity.

<Step (5)>

[0100] In the step (5), the dispersion of the toner base particles is cooled, and the toner base particles are separated from the dispersion of the toner base particles by solid-liquid separation. The toner cake obtained by the solid-liquid separation (toner base particles in a wet state formed into a cake shape) is washed by removing attached substances such as a surfactant and an aggregating agent, and the washed toner cake is dried.

<Step (6)>

[0101] In the step (6), an external additive is added to the toner base particles. In particular, adding the external additive by the split mixing method is capable of controlling the adhesive strength to the toner base particles for each type of the external additive. It is preferable that the free external additive may be adjusted so as to satisfy the relationship of the following expression (3) or expression (4).

$$\text{Expression (3): } 0.5 \leq ([\mathrm{Si}] + [\mathrm{Ti}] + [\mathrm{Ca}] + [\mathrm{Al}] + [\mathrm{Sr}]) / [\mathrm{Zn}]) \leq 2.5$$

$$\text{Expression (4): } 3.5 \leq ([\mathrm{Si}] + [\mathrm{Ti}] + [\mathrm{Ca}] + [\mathrm{Al}] + [\mathrm{Sr}]) / [\mathrm{Zn}]) \leq 8.0$$

[0102] The first mixing time in the split mixing method is preferably in the range of 10 to 25 minutes, more preferably in the range of 15 to 20 minutes. Further, the second mixing time is preferably in the range of 1 to 10 minutes, more preferably in the range of 2 to 6 minutes. Within this range, the adhesion strength may be easily adjusted by changing the timing of adding the external additive in order to achieve both the fixing property, the heat resistance, and the fluidity. The amount of the external additive added in the first mixing in the split mixing method is preferably 0.1 to 1.0 part by mass, and preferably 0.1 to 0.5 part by mass with respect to 100 parts by mass of the toner base particles. The amount of the external additive added in the second mixing is preferably from 0.0 to 1.2 parts by mass, more preferably from 0.1 to 0.6 parts by mass, based on 100 parts by mass of the toner base particles. Within this range, it is easy to adjust the adhesion strength by changing the amount of the external additive added in order to achieve both fixing properties, heat resistance and fluidity.

[0103] For adding the external additive, a mechanical mixing device such as a Henschel mixer or a coffee mill can be used.

[Developer]

[0104] The electrostatic image developing toner of the present invention may be used as a magnetic or nonmagnetic one-component developer, and may be mixed with a carrier and used as a two-component developer. When the toner is used as a two-component developer, the magnetic particles made of known materials may be used as a carrier. Examples the carrier includes a ferromagnetic metal such as iron, an alloy of a ferromagnetic metal with aluminum and lead, a compound of a ferromagnetic metal such as ferrite and magnetite. Ferrite is particularly preferable.

[0105] The carrier particles may be coated carrier particles obtained by coating the surfaces of magnetic particles with a coating agent such as a resin, or resin-dispersed carrier particles in which magnetic powder is dispersed in a binder resin. The volume-based median diameter of the carrier particles is preferably in the range of 20 to 100 μm, and more preferably in the range of 25 to 80 μm. The volume-based median diameter of the carrier particles may be typically measured by a laser diffraction particle size distribution measuring apparatus "HELOS" (manufactured by SYMPATEC Co., Ltd.) equipped with a wet disperser.

[Image forming method]

[0106] The image forming method of the present invention is an image forming method using an electrostatic image developing toner including toner particles comprising at least toner base particles and an external additive, wherein the content of titanium oxide as the external additive is 1 part by mass or less based on 100 parts by mass of the toner base particles, and an amount of metal [A] (CPS) on a surface of a photoreceptor which is measured by X-ray photoelectron spectroscopy after printing 5,000 sheets at 20% coverage on A4 high-quality paper (basis weight: 68 g/m^2) in an environment of 30 °C and 80% RH and a photoreceptor wear α value [B] satisfy a relationship of the following expression (1) or expression (2),

$$\text{Expression (1): } 30{,}000 \leq [A] \leq 50{,}000$$

$$\text{Expression (2): } 2.50 \leq [B] \leq 5.00.$$

[0107] In order for the metal amount [A] on the photoreceptor surface and the photoreceptor wear α value [B] to satisfy the relationship of the above expression (1) or expression (2), as described above, in the step of adding the external additive to the toner, it is preferable to add the external additive to the toner base particles by the split mixing method.

[0108] The image forming method of the present invention is preferably a general electrophotographic image forming method, and preferably has at least a charging step, a latent image forming step, a developing step, a transfer step, a fixing step, and a cleaning step.

<Charging step>

[0109] In this step, an electrophotographic photoreceptor is charged. The charging method is not particularly limited, and, for example, a charging unit described below may be suitably used.

<Latent image forming step>

[0110] In this step, an electrostatic latent image is formed on the electrophotographic photoreceptor (electrostatic latent image carrier). The electrophotographic photoreceptor is not particularly limited, and examples thereof include a drum-shaped electrophotographic photoreceptor made of an organic photoreceptor such as polysilane or phthalopolymethine. The formation of the electrostatic latent image is performed by uniformly charging the surface of the electrophotographic photoreceptor by a charging unit and exposing the surface of the electrophotographic photoreceptor imagewise by an exposing unit, as described later. The exposure means is not particularly limited, and those described later may be used.

<Developing step>

[0111] The developing step is a step of developing the electrostatic latent image with a dry developer containing toner to form a toner image. The formation of the toner image is performed using a dry developer containing a toner, for example, using a developing unit described below. More specifically, in the developing unit, for example, the toner and the carrier are mixed and stirred, and the toner is charged by friction at that time, and is held on the surface of the rotating magnet roller to form a magnetic brush. Since the magnet roller is disposed near the electrophotographic photoreceptor, a part of the toner constituting the magnetic brush formed on the surface of the magnet roller moves to the surface of the electrophotographic photoreceptor by an electric attraction force. As a result, the electrostatic latent image is developed by the toner, and a toner image is formed on the surface of the electrophotographic photoreceptor.

<Transfer step>

[0112] In this step, the toner image is transferred to the transfer material. The transfer of the toner image to the transfer material is performed by peel-charging the toner image on the transfer material. As the transfer means, for example, a corona transfer device using corona discharge, a transfer belt, and a transfer roller may be used. In the transfer step, for example, an intermediate transfer unit (intermediate transfer body) is used, and a toner image is primarily transferred onto the intermediate transfer body, and then this toner image is secondarily transferred onto a transfer material. It may also be performed by an embodiment in which the toner image formed on the electrophotographic photoreceptor is directly transferred to a transfer material. The transfer material is not particularly limited, various types of materials such as plain paper from thin paper to thick paper, high-quality paper, coated printing paper such as art paper or coated paper, commercially available Japanese paper and postcard paper, OHP plastic film, and cloth may be mentioned.

<Fixing step>

[0113] In the fixing step, the toner image transferred to the transfer material is fixed to the transfer material. The fixing method is not particularly limited, and a known fixing unit as described later can be used. Specifically, for example, a heat roller fixing device configured by a heating roller having a heating source therein, and a pressure roller provided in a state of being pressed against the heating roller so as to form a fixing nip portion may be mentioned.

<Cleaning step>

[0114] In this step, the developer not used for image formation or remaining without being transferred on the developer carrier such as a developing roller, a photoreceptor, and an intermediate transfer body is removed from the developer carrier. The cleaning method is not particularly limited, but it is preferably a method using a blade that rubs the surface of the photoreceptor, and the tip of which is provided in contact with the photoreceptor. For example, a cleaning unit as described later may be used. In the cleaning step, it is preferable to clean the intermediate transfer body using a white toner for developing an electrostatic image. In this method, the white toner for developing an electrostatic image is transferred to the non-image forming area of the intermediate transfer body corresponding to the space between the transfer materials that are continuously transported, and the white toner for developing the electrostatic image is collected by a cleaning unit such as a blade.

[Image forming apparatus]

[0115] The figure illustrates, as an example, an image forming apparatus used in the image forming method of the present invention. The image forming apparatus includes a charging unit, an electrostatic image forming unit, a developing unit, a transfer unit, a fixing unit, and a cleaning unit, and the developing unit includes the electrostatic image developing toner of the present invention. It is preferable that the developing unit develops an electrostatic image with a developer for developing an electrostatic image containing the toner for developing an electrostatic image of the present invention to form a toner image. Further, the image forming apparatus has at least five electrostatic image forming units and five or more developing units. For example, an electrostatic image forming unit and a developing unit corresponding to five colors of white (W), yellow (Y), magenta (M), cyan (C) and black (Bk) are provided for each color. This is preferable because a full-color image realizing a white color having concealing properties, hue, and transferability that will meet the demands of the production print market may be formed.

[0116] This image forming apparatus 100 is called a tandem type color image forming apparatus. It contains five sets of image forming sections (image forming units) 10W, 10Y, 10M, 10C, and 10Bk, an endless belt-shaped intermediate transfer unit 7, a sheet feeding unit 21, and a fixing unit 24. A document image reading device SC is arranged above the main body A of the image forming apparatus 100.

[0117] The image forming unit 10W for forming a white image has a drum-shaped photoreceptor 1W, a charging unit 2W, an exposing unit 3W, a developing unit 4W, a primary transfer roller 5W as a primary transfer unit, and a cleaning unit 6W. The image forming unit 10Y for forming a yellow image includes a charging unit 2Y, an exposing unit 3Y, a developing unit 4Y, a primary transfer roller 5Y as a primary transfer unit, and a cleaning unit 6Y disposed around the drum-shaped photoreceptor 1Y. The image forming unit 10M for forming a magenta image has a drum-shaped photoreceptor 1M, a charging unit 2M, an exposing unit 3M, a developing unit 4M, a primary transfer roller 5M as a primary transfer unit, and a cleaning unit 6M. The image forming section 10C for forming a cyan image has a drum-shaped photoreceptor 1C, a charging unit 2C, an exposing unit 3C, a developing unit 4C, a primary transfer roller 5C as a primary transfer unit, and a cleaning unit 6C. The image forming unit 10Bk for forming a black image has a drum-shaped photoreceptor 1Bk, a charging unit 2Bk, an exposing unit 3Bk, a developing unit 4Bk, a primary transfer roller 5Bk as a primary transfer unit, and a cleaning unit 6Bk.

[0118] Five image forming units (10W, 10Y, 10M, 10C and 10Bk) each respectively configured to have the photoreceptors 1W, 1Y, 1M, 1C, and 1Bk as the centers, the charging units 2W, 2Y, 2M, 2C, and 2Bk, the exposure units 3W, 3Y, 3M, 3C, and 3Bk that are the electrostatic image forming units, and the rotation developing units 4W, 4Y, 4M, 4C and 4Bk, and cleaning units 6W, 6Y, 6M, 6C and 6Bk for cleaning the photoreceptors 1W, 1Y, 1M, 1C and 1Bk.

[0119] The image forming units 10W, 10Y, 10M, 10C, and 10Bk have the same configuration except that the colors of the toner images formed on the photoreceptors 1W, 1Y, 1M, 1C, and 1Bk are different. Hereinafter, the image forming unit 10W will be described in detail as an example.

[0120] In the image forming unit 10W, a charging unit 2W, an exposing unit 3W, a developing unit 4W, and a cleaning unit 6W are arranged around a photoreceptor 1W which is an image forming body, and a white (W) toner image is formed on the photoreceptor 1W. Further, in the present embodiment, in the image forming unit 10W, at least the photoreceptor 1W, the charging unit 2W, the developing unit 4W, and the cleaning unit 6W are provided so as to be integrated.

[0121] The charging unit 2W is a unit that applies a uniform potential to the photoreceptor 1W. In the present invention, examples of the charging unit include a contact or non-contact roller charging system.

[0122] The exposure unit 3W is a unit that performs exposure based on an image signal (white) on the photoreceptor 1W to which a uniform potential is applied by the charging unit 2W, and forms an electrostatic latent image corresponding to a white image. As the exposure unit 3W, for example, a device composed of an LED having light emitting elements arranged in an array in the axial direction of the photoreceptor 1W and an imaging element, or a laser optical system is used.

[0123] The developing unit 4W includes, for example, a developing sleeve that contains a magnet and rotates while holding the developer, and a voltage applying device that applies a DC and/or AC bias voltage between the photoreceptor 1Y and the developing sleeve. In particular, it is preferable that the developing unit 4W develops the electrostatic image with the electrostatic image developing developer containing the white toner for electrostatic image development of the present invention to form a toner image.

[0124] The fixing unit 24 includes, for example, a heat roller fixing unit including a heating roller having a heating source therein, and a pressure roller provided in a state in which the heating roller is pressed against the heating roller so as to form a fixing nip portion.

[0125] The cleaning unit 6W includes a cleaning blade and a brush roller provided upstream of the cleaning blade.

[0126] The image forming apparatus 100 may be configured by integrally combining components such as a photoreceptor, a developing unit, and a cleaning unit as a process cartridge (image forming unit). This image forming unit may be configured to be detachable from the apparatus main body. Also, a process cartridge (image forming unit) may be formed by integrally supporting at least one of a charging unit, an exposing unit, a developing unit, a transferring unit, and a cleaning unit together with a photoreceptor, and a single image forming unit that is detachable from the apparatus main body may be made. This single image forming unit may be configured to be detachable using a guide means such as a rail of the apparatus main body.

[0127] The endless belt-shaped intermediate transfer body unit 7 has an endless belt-shaped intermediate transfer body 70 as a semiconductive endless belt-shaped second image carrier rotatably supported by a plurality of rollers.

[0128] Images of each color formed by the image forming units 10W, 10Y, 10M, 10C and 10Bk are sequentially transferred onto the rotating endless belt-shaped intermediate transfer body 70 by the primary transfer rollers 5W, 5Y, 5M, 5C and 5Bk as primary transfer means. Thus, a combined color image is formed. A transfer material (an image support that carries a fixed final image: plain paper or a transparent sheet) P accommodated in the paper feed cassette 20 is fed by a paper feed unit 21. It is transported to a secondary transfer roller 5b as a secondary transfer means via a plurality of intermediate rollers 22A, 22B, 22C, 22D and a registration roller 23, and the images are secondarily transferred onto the transfer material P, and the color images are collectively transferred. The transfer material P to which the color image has been transferred is subjected to a fixing process by a fixing unit 24, and it is sandwiched by sheet discharge rollers 25 and placed on a sheet discharge tray 26 outside the apparatus. Here, a transfer support for a toner image formed on a photoreceptor such as an intermediate transfer member or a transfer material is collectively referred to as a transfer medium.

[0129] On the other hand, after the color image is transferred onto the transfer material P by the secondary transfer roller 5b as a secondary transfer means, the endless belt-shaped intermediate transfer body 70, from which the transfer material P is separated by curvature, is removed the residual toner by the cleaning means 6b.

[0130] During the image forming process, the primary transfer roller 5Bk is always in contact with the photoreceptor 1Bk. The other primary transfer rollers 5W, 5Y, 5M, and 5C contact the corresponding photoreceptors 1W, 1Y, 1M, and 1C only during color image formation.

[0131] The primary transfer roller 5W may be brought into contact with the photoreceptor 1W to develop and transfer the toner for developing an electrostatic image of the present invention to the intermediate transfer member 70 even when the image is not formed. Normally, an image is not formed between the transfer materials P which are continuously conveyed. Therefore, the toner image of each color is not transferred to the non-image forming area of the endless belt-shaped intermediate transfer body 70 corresponding to between the transfer materials P. The toner for developing an electrostatic image of the present invention is developed and transferred to the non-image forming area of the endless belt-shaped intermediate transfer body 70. This toner is naturally not transferred to the transfer material P, so that the toner is held on the endless belt-shaped intermediate transfer body 70 without being transferred by the secondary transfer roller 5b, and then removed by the cleaning unit 6b.

[0132] The secondary transfer roller 5b abuts on the endless belt-shaped intermediate transfer body 70 only when the transfer material P passes here and the secondary transfer is performed.

[0133] Further, the housing 8 can be pulled out from the apparatus main body A via the support rails 82L and 82R.

[0134] The housing 8 includes the image forming units 10W, 10Y, 10M, 10C, and 10Bk, and an endless belt-shaped intermediate transfer body unit 7.

[0135] The image forming units 10W, 10Y, 10M, 10C and 10Bk are arranged in tandem in the vertical direction. An endless belt-shaped intermediate transfer body unit 7 is disposed on the left side of the photoreceptors 1W, 1Y, 1M, 1C and 1Bk in the drawing. The endless-belt-shaped intermediate transfer body unit 7 includes an endless-belt-shaped intermediate transfer body 70 that can rotate around rollers 71, 72, 73, and 74, primary transfer rollers 5W, 5Y, 5M, 5C, and 5Bk, and cleaning means 6b.

[0136] Although a color laser printer is indicated in the image forming apparatus 100 illustrated in the figure, the present invention is similarly applicable to a monochrome laser printer and a copying machine. Also, a light source other than a laser, for example, an LED light source may be used as the exposure light source.

[0137] The embodiments to which the present invention may be applied are not limited to the above-described embodiments, and changes may be made as appropriate without departing from the spirit of the present invention. The scope of the present invention should be interpreted by terms of the appended claims.

EXAMPLES

[0138] Hereinafter, the present invention will be described specifically with reference to Examples, but the present invention is not limited thereto.

[Dispersion liquid of styrene-acrylic resin particles]

(1) First stage polymerization

[0139] Into a reaction vessel equipped with a stirrer, a temperature sensor, a cooling tube, and a nitrogen introducing device, an anionic surfactant solution prepared by dissolving 2.0 parts by mass of sodium lauryl sulfate as anionic surfactant in 2900 parts by mass of ion-exchanged water was charged. While stirring at a stirring speed of 230 rpm under a nitrogen flow, the inner temperature of the reaction vessel was raised to 80 °C. 9.0 parts by mass of potassium persulfate (KPS) as a polymerization initiator was added to the surfactant solution, and the internal temperature was set to 78 °C. The following polymerizable monomer solution was added dropwise to this solution over 3 hours. After dropping the monomer mixture, the reaction system was heated and stirred at 78 °C for 1 hours to carry out the polymerization (first stage polymerization). Thus, a dispersion liquid (I) of styrene-acrylic resin particles was prepared.

Styrene:	540 parts by mass
N-Butyl acrylate:	270 parts by mass
Methacrylic acid:	65 parts by mass
N-octyl mercaptan:	17 parts by mass

(Second stage polymerization)

[0140] In a flask equipped with a stirrer, 50 parts by mass of a hydrocarbon wax (melting point: 78 °C) as a release agent is added to a monomer solution having the following composition, and the wax is dissolved by heating to 85 °C to prepare a wax solution.

Styrene:	94 parts by mass
N-butyl acrylate:	30 parts by mass

2-ethylhexyl acrylate: 30 parts by mass
Methacrylic acid: 11 parts by mass
N-octyl mercaptan: 5 parts by mass

[0141] On the other hand, a surfactant solution obtained by dissolving 2 parts by mass of sodium lauryl sulfate as an anionic surfactant in 1100 parts by mass of ion-exchanged water was heated to 90 °C. To this surfactant solution, 28 parts by mass of the dispersion liquid (I) of styrene-acrylic resin particles in terms of solid content of styrene-acrylic resin was added. Thereafter, the wax solution was mixed and dispersed for 1 hour using a mechanical disperser CLEARMIX (manufactured by M Technic Co., Ltd.) having a circulation path to prepare a dispersion containing emulsified particles having a dispersed particle diameter of 350 nm. An aqueous solution of a polymerization initiator obtained by dissolving 2.5 parts by mass of potassium persulfate (KPS) as a polymerization initiator in 110 parts by mass of ion-exchanged water was added to the dispersion, and the mixture was heated and stirred at 90 °C for 2 hours. Thus, polymerization (second stage polymerization) was performed to prepare a dispersion liquid (II) of styrene-acrylic resin particles.

(Third stage polymerization)

[0142] To the prepared dispersion liquid (II) of styrene-acrylic resin particles, an aqueous solution of a polymerization initiator obtained by dissolving 2.5 parts by weight of potassium persulfate (KPS) as a polymerization initiator in 110 parts by weight of ion-exchanged water was added. Under a temperature condition of 80 °C, a monomer solution having the following composition was dropped over 1 hour. After completion of the dropwise addition, polymerization (third stage polymerization) was performed by heating and stirring for 3 hours.

Styrene: 230 parts by mass
N-butyl acrylate: 100 parts by mass
Methacrylic acid: 19 parts by mass
N-octyl mercaptan: 5 parts by mass

[0143] Thereafter, the mixture was cooled to 28 °C to obtain a dispersion of styrene-acrylic resin particles. The weight average molecular weight (Mw) of the styrene-acrylic resin in this dispersion liquid was 33,100, and the number average molecular weight (Mn) was 10,900.

[Preparation of dispersion liquid 1 of crystalline polyester resin particles]

[0144] In a 5 L reaction vessel equipped with a stirrer, a temperature sensor, a cooling tube, and a nitrogen introduction device, 383 parts by mass of 1,12-dodecanedicarboxylic acid (tetradecandioic acid) as a polyvalent carboxylic acid and 237 parts by mass of 1,9-nonanediol as a polyhydric alcohol were added. The internal temperature was raised to 190 °C over 1 hour while stirring. After confirming that the mixture was uniformly stirred, $Ti(OBu)_4$ was added as a catalyst in an amount of 0.003% by mass based on the charged amount of the polyvalent carboxylic acid. The internal temperature was raised from 190 °C to 240 °C over 6 hours while distilling off the generated water, and the dehydration-condensation reaction was continued for 6 hours at a temperature of 240 °C to carry out polymerization, thereby a crystalline polyester resin 1 was obtained. The melting point (Tm) of this crystalline polyester resin 1 was 67.2 °C, and the number average molecular weight (Mn) was 6,600.

[0145] Into a 3-liter reaction vessel equipped with a cooling tube, a thermometer, a water dropping device and an anchor fin (BJ-30N, Tokyo Rikakikai Co., Ltd.), 300 parts by mass of the above-described crystalline polyester resin, 160 parts by mass of methyl ethyl ketone (solvent) and 100 parts by mass of isopropyl alcohol (solvent) were charged. The resin was dissolved while stirring and mixing at 100 rpm with maintaining the temperature at 70 °C in a water circulation type thermostat bath. Thereafter, the stirring speed was changed to 150 rpm, the water circulating thermostat bath was set to 66 °C and 17 parts by mass of 10 mass% aqueous ammonia (reagent) was added over 10 minutes. Then, 900 parts by mass in total of ion-exchanged water maintained at 66 °C was added dropwise at a rate of 7 parts by mass per minute to cause phase inversion so that emulsion was obtained. Immediately, 800 parts by mass of the emulsion thus obtained and 700 parts by mass of ion-exchanged water were charged into a 2-L eggplant flask, and the flask was set to an evaporator equipped with a vacuum control unit (Tokyo Rikakikai, Co., Ltd) via a ball trap. While being rotated, the eggplant flask was heated in a water bath at 60 °C. The pressure was reduced to 7 kPa with careful attention in order to avoid bumping so that the solvent was removed. The pressure was increased to ordinary pressure when the amount of solvent collected reached 1100 parts by mass, and the eggplant flask was cooled by water so that the dispersion liquid was obtained. The dispersion liquid thus obtained did not have solvent odor. The volume-based median diameter (D_{50}) of the resin particles in this dispersion liquid was 120 nm. Thereafter, ion-exchanged water was added to adjust the solid content to 20% by mass, and this was used as a dispersion liquid 1 of crystalline polyester resin particles.

[Dispersion liquid of amorphous polyester resin particles]

[0146] Into a 10-liter four-necked flask equipped with a nitrogen inlet tube, a dehydrating tube, a stirrer, and a thermocouple, 500 parts by mass of bisphenol A propylene oxide 2 mol adduct, 108 parts by mass of terephthalic acid, 80 parts by mass of fumaric acid, 12 parts by mass of trimelitic acid, 15 parts by mass of dodecenylsuccinic anhydride and 2 parts by mass of an esterification catalyst (tin octylate) were loaded. A polycondensation reaction was performed at 230 °C for 8 hours, and further a reaction was performed at 8 kPa for 1 hour to obtain an amorphous polyester resin. This amorphous polyester resin had a glass transition point (Tg) of 58 °C, a softening point (Tsp) of 101 °C, and a weight average molecular weight (Mw) of 27,000.

[0147] Then, a 3-liter reaction vessel with a jacket (BJ-30N, manufactured by Tokyo Rika Instruments Co., Ltd.) equipped with a cooling tube, a thermometer, a water dropping device, and an anchor blade was maintained at 40 °C in a water circulation type thermostat bath. A mixed solvent of 160 parts by mass of ethyl acetate and 100 parts by mass of isopropyl alcohol was charged into the reaction vessel. Further, 300 parts by mass of the amorphous polyester resin was charged, and the mixture was stirred at 150 rpm by a three-one motor and dissolved to obtain an oil phase. To the stirred oil phase, 14 parts by mass of a 10% by mass aqueous ammonia solution was dropped for 5 minutes, and after mixing for 10 minutes, 900 parts by mass of ion-exchanged water was dropped at a rate of 7 parts by minute. The phase was inverted to obtain an emulsion. Immediately, 800 parts by mass of the emulsion thus obtained and 700 parts by mass of ion-exchanged water were charged into a 2-L eggplant flask, and the flask was set to an evaporator equipped with a vacuum control unit (Tokyo Rikakikai, Co., Ltd) via a ball trap. While being rotated, the eggplant flask was heated in a water bath at 60 °C. The pressure was reduced to 7 kPa with careful attention in order to avoid bumping so that the solvent was removed. The pressure was increased to ordinary pressure when the amount of solvent collected reached 1100 parts by mass, and the eggplant flask was cooled by water so that the dispersion liquid was obtained. The dispersion liquid thus obtained did not have solvent odor. The volume-based median diameter (D_{50}) of the resin particles in this dispersion liquid was 140 nm. Thereafter, ion-exchanged water was added to adjust the solid content to 20% by mass, thus a dispersion liquid 1 of amorphous polyester resin particles.

[Dispersion liquid of colorant particles]

[0148] 90 parts by mass of sodium dodecyl sulfate was dissolved in 1600 parts by mass of ion-exchanged water while stirring, and 420 parts by mass of copper phthalocyanine was gradually added while stirring the solution. Next, a dispersion liquid of colorant particles was prepared by performing a dispersion treatment using a stirrer CLEARMIX (manufactured by M Technique Co., Ltd.). The average particle size of the colorant particles in the dispersion liquid was 110 nm as a volume-based median diameter.

[Production of Toner (1)]

[0149] Into a reaction vessel equipped with a stirrer, a temperature sensor, and a cooling tube, 280 parts by mass of the dispersion of the above-described styrene-acrylic resin particles in terms of solid content and 2,000 parts by mass of ion-exchanged water were charged. The pH was adjusted to 10 by adding a 5 mol/liter aqueous sodium hydroxide solution. Next, an aqueous solution in which 60 parts by mass of magnesium chloride was dissolved in 60 parts by mass of ion-exchanged water was added over 10 minutes at 30 °C with stirring. After standing for 3 minutes, heating was started, and the system was heated to 80 °C over 60 minutes. Then, 40 parts by mass of the dispersion liquid 1 of crystalline polyester resin particles in terms of solid content was added over 30 minutes, and the core particle growth reaction was continued while maintaining the temperature at 80 °C. In this state, the particle size of the core particle was measured with a particle size distribution measuring device ("MULTISIZER 3", manufactured by Coulter Beckman). When the number-based median diameter (D_{50}) reaches 6.0 μm, 40 mass parts (in terms of solid content) of the dispersion liquid of amorphous polyester resin particles was added over 30 minutes to obtain a shell layer. At the point that the supernatant of the reaction solution became transparent, an aqueous solution in which 190 mass parts of sodium chloride was dissolved in 760 mass parts of ion-exchanged water was added to stop particle growth. Further, the temperature was raised and the mixture was heated and stirred at 90 °C to advance the fusion of the particles. Using an apparatus for measuring the average circularity of toner base particles ("FPIA-2100", manufactured by Sysmex) (the number of HPF detection was measured as 4000), when the average circularity reached 0.960, the system was cooled to 30 °C. Thus, an aqueous dispersion of toner base particles having a core-shell structure was obtained. The aqueous dispersion of toner base particles was subjected to solid-liquid separation with a centrifuge to form a wet cake of toner base particles. This wet cake was washed with ion exchange water at 35 °C until the electric conductivity of the filtrate reached 5 μS/cm, and then transferred to an airflow dryer "Flash Jet Dryer" (manufactured by Seishin Enterprise Co., Ltd.). It was dried to 0.5 mass% to obtain toner base particles (1). 100 parts by mass of the toner base particles (1) and the following first mixed material were added to a Henschel mixer type "FM20C/I" (manufactured by Nippon Coke Industry Co., Ltd.) so that the blade tip peripheral speed becomes 38 m/sec. The mixture was stirred for 19 minutes at a set rotation speed. Subsequently, the following second mixed material was added to the Henschel mixer, and the mixture was further stirred for 2 minutes without changing the rotation speed. The temperature of the powder mixture during stirring was set to be 40 °C ± 1 °C. When the temperature reaches 41 °C, the cooling water was poured into the outer bath of the Henschel mixer at a flow rate of 5 L/min. When the temperature reaches 39 °C, the cooling water was poured at a flow rate of 1 L/min. The temperature inside the mixer was controlled. Thus, a toner (1) was obtained.

<First mixed material >

[0150]

Hydrophobic silica particles 1:	0.3 parts by mass
Hydrophobic silica particles 2:	0.9 parts by mass
Hydrophobic silica particles 3:	0.4 parts by mass
Calcium titanate particles:	0.3 parts by mass
Zinc stearate particles:	0.1 parts by mass

<Second mixed material>

[0151]

Hydrophobic aluminum oxide particles:	0.5 parts by mass

[0152] The "hydrophobic silica particles 1" are silica particles surface-modified with hexamethyldisilazane (HMDS), have a hydrophobicity of 72%, and a number average primary particle diameter of 80 nm. The "hydrophobic silica particles 2" are silica particles surface-modified with hexamethyldisilazane (HMDS), have a hydrophobicity of 58%, and a number average primary particle diameter of 30 nm. The "hydrophobic silica particles 3" are silica particles surface-modified with hexamethyldisilazane (HMDS), have a hydrophobicity of 67%, and a number average primary particle diameter of 16 nm. The "calcium titanate particles" are calcium titanate particles surface-modified with silicone oil, and have a number-average primary particle diameter of 100 nm. The "hydrophobic aluminum oxide particles" are aluminum oxide particles surface-modified with alkylsilane (carbon number 4), have a hydrophobicity of 67%, and a number average primary particle diameter of 13 nm. The "zinc stearate particles" have a number average primary particle size of 1.5 μm or less.

[Production of Toners (2) to (13) and (17) to (21)]

[0153] Toners (2) to (13) and (17) to (21) were prepared in the same manner as in the production of the toner (1) except that the addition amount and the mixing timing of the calcium titanate particles and the zinc stearate particles were changed as indicated in the following table I.

[Production of Toner (14)]

[0154] Toner (14) was prepared in the same manner as in the production of Toner (1) except that 0.3 parts by mass of strontium titanate particles were added to the first mixture. The "strontium titanate particles" are strontium titanate particles surface-modified with isobutyltrimethoxysilane, have a hydrophobicity of 61%, and a number average primary particle diameter of 90 nm.

[Production of Toner (15)]

[0155] Toner (15) was prepared in the same manner as in the production of Toner (1) except that zinc stearate particles in the first mixed material were replaced with magnesium stearate particles. The "magnesium stearate particles" have a number average primary particle diameter of 1.5 μm or less.

[Production of Toner (16)]

[0156] 100 parts by mass of the toner base particles (1) and the following first mixed material are added to a Henschel mixer type "FM20C/I" (manufactured by Nippon Coke Industry Co., Ltd.) so that the blade tip peripheral speed became 40 m/sec. The mixture was stirred for 19 minutes at a set rotation speed.

<First mixed material>

[0157]

Hydrophobic silica particles 2:	0.9 parts by mass
Hydrophobic silica particles 4:	0.6 parts by mass
Calcium titanate particles:	0.3 parts by mass
Zinc stearate particles:	0.1 parts by mass

<Second mixed material>

[0158]

Hydrophobic titanium oxide particles 1:	0.4 parts by mass
Hydrophobic titanium oxide particles 2:	0.5 parts by mass

[0159] The "hydrophobic silica particles 4" are silica particles surface-modified with alkylsilane (carbon number 8), have a hydrophobicity of 72%, and a number average primary particle diameter of 12 nm. The "hydrophobic titanium oxide particles 1" are titanium oxide particles surface-modified with isobutylsilane, have a hydrophobicity of 63%, and a number average primary particle diameter of 20 nm. The "hydrophobic titanium oxide particles 2" are titanium oxide particles surface-modified with alkylsilane (carbon number 8), have a hydrophobicity of 73%, and a number average primary particle diameter of 100 nm.

<Amount of metal on photoreceptor surface>

[0160] Using each of the toners obtained above, the amount of metal [A] on the surface of the photoreceptor was calculated. Specifically, using an X-ray photoelectron spectroscopy analyzer "K-Alpha" (manufactured by Thermo Fisher Scientific Inc.), quantitative analysis of metal atoms was performed under the following conditions. The surface element concentration in the range of the outermost surface of the photoreceptor and within 3 nm in the depth direction from the outermost surface were calculated. The results are shown in the table below.

(Measurement condition)

[0161]

X-ray:	Almonochromatic X-ray source
Acceleration:	12 kV, 6 mA
Resolution:	50 eV
Beam diameter:	400 μm
Pass energy:	50 eV
Step size:	0.1 eV

<Wear amount of photoreceptor >

[0162] When each of the toners obtained above was used to print 5,000 sheets at a coverage of 20% on A4 high-quality paper (basis weight: 68 g/m^2) under an environment of 30 °C and 80 %RH, the uniform thickness portion of the photoreceptor (except for at least 3 cm at both ends of the photoreceptor because the film thickness tends to be non-uniform) before and after the endurance test was measured with an eddy current type film thickness measuring device (EDDY560C; manufactured by HELMUT FISCHER GMBTE CO.) was used. The measurement was carried out at 10 random points, and the average value was determined to be the thickness of the layer on the photoreceptor. The difference between the thicknesses of the layers before and after the durability test was defined as the amount of wear, and based on the rotation number of the photoreceptor when 5,000 sheets were printed, the amount of wear per 100,000 rotations of the photoreceptor was determined and defined as the photoreceptor wear α value [B]. The results are indicated in the table below. It was determined that there was no practical problem when the α value [B] was 5.0 μm or less.

(Evaluation criteria)

[0163]

AA α value is 3.0 μm or less

BB: α value is larger than 3.0 μm and not more than 4.0 μm

CC: α value is larger than 4.0 μm and not more than 5.0 μm

DD: α value is larger than 5.0 μm

[Evaluation]

<Attached substance on photoreceptor (raindrop)>

[0164] As an evaluation machine (electrophotographic image forming apparatus), a digital color MFP "bizhub C658" modified machine (manufactured by Konica Minolta, Inc.) was used. In an environment of a temperature of 30 °C and a humidity of 80 %RH, 5,000 sheets of 20% coverage horizontal band charts were output on A4 quality paper (basis weight: 68 /m^2). Thereafter, the photoreceptor unit was removed from the electrophotographic image forming apparatus, and the number of raindrops generated for one round of the photoreceptor having a diameter of 30 mm and a length of 360 mm (area conversion: 33929 mm2) was visually observed. When the number of raindrops was 0 to 30, it was determined that there was no problem in practical use.

<Wear amount of cleaning blade>

[0165] After the above-described endurance, the cleaning blade was removed from the electrophotographic image forming apparatus, and the photoreceptor contact portion was observed using a laser microscope VK9500 (magnification: 150 times, observation width: 700 μm). The width of the smooth portion that appeared due to abrasion at the photoreceptor contact portion was measured as the wear amount (μm) of the cleaning blade. It was determined that there was no practical problem when the wear amount of the cleaning blade was 6.5 μm or less.

(Evaluation criteria)

[0166]

AA Wear amount is 2.5 μm or less
BB: Wear amount is larger than 2.5 μm and not more than 6.0 μm
CC: Wear amount is larger than 6.0 μm and not more than 6.5 μm
DD: Wear amount is larger than 6.5 μm

Table I

Toner No.	Titanium oxide	Strontium titanate	Added Amount of calcium titanate (part by mass)		Added amount of zinc stearate (part by mass)		Added amount of magnesium stearate (part by mass)	Amount of metal [A] (CPS) on photoreceptor surface	Photoreceptor wear α value [B] (μm)		*1	*2	Wear amount of cleaning blade (μm)		Remarks
			*3	*4	*3	*4	*3								
1	Absent	Absent	0.3	0	0.1	0	0	2723	2.54	AA	6.3	0	3.14	BB	*5
2	Absent	Absent	0	0.5	0.1	0	0	2019	3.80	BB	7.4	0	2.23	AA	*5
3	Absent	Absent	0	1	0.1	0	0	1121	4.90	CC	8	0	1.43	AA	*5
4	Absent	Absent	0.1	0	0	0.3	0	31084	0.95	AA	2.5	20	5.21	BB	*5
5	Absent	Absent	0.1	0	0	0.6	0	39649	0.88	AA	1	10	5.69	BB	*5
6	Absent	Absent	0.1	0	0	1	0	49120	0.65	AA	0.5	0	6.42	CC	*5
7	Absent	Absent	0.6	0	0.3	0	0	3520	2.60	AA	4	0	4.32	BB	*5
8	Absent	Absent	0.6	0	0.4	0	0	3933	2.50	AA	3.9	25	4.63	BB	*5
9	Absent	Absent	0	1.2	0.2	0	0	923	5.00	CC	8.1	0	1.48	AA	*5
10	Absent	Absent	0	1.1	0.2	0	0	1042	4.95	CC	8	0	1.51	AA	*5
11	Absent	Absent	0	0	0	0.3	0	30285	0.51	AA	2.6	30	6.35	CC	*5
12	Absent	Absent	0.1	0	0	1.1	0	49883	0.60	AA	0.4	5	6.5	CC	*5
13	Absent	Absent	0	0.7	0.05	0	0	0	5.00	CC	8.2	0	0.88	AA	*5
14	Absent	Present	0.3	0	0.1	0	0	1892	3.96	BB	7.6	0	2.11	AA	*5
15	Absent	Absent	0.3	0	0	0	0.1	1821	3.88	BB	-	0	2.15	AA	*5
16	Present	Absent	0.3	0	0.1	0	0	776	5.58	DD	9.4	0	1.28	AA	*6
17	Absent	Absent	0	0.3	0.3	0	0	3574	2.40	AA	3.8	40	4.91	BB	*6
18	Absent	Absent	0.3	0	0.3	0	0	4258	2.20	AA	2.8	520	5.01	BB	*6
19	Absent	Absent	0	1.1	0.1	0	0	803	5.12	DD	8.3	0	1.28	AA	*6
20	Absent	Absent	0.1	0	0	1.2	0	50252	0.48	AA	0.2	0	6.77	DD	*6

(continued)

Toner No.	Titanium oxide	Strontium titanate	Added Amount of calcium titanate (part by mass)		Added amount of zinc stearate (part by mass)		Added amount of magnesium stearate (part by mass)	Amount of metal [A] (CPS) on photoreceptor surface	Photoreceptor wear α value [B] (μm)		*1	*2	Wear amount of cleaning blade (μm)		Remarks
			*3	*4	*3	*4	*3								
21	Absent	Absent	0.1	0	0	0.2	0	29730	1.21	AA	2.7	60	4.95	BB	*6

*1:Free external additives ratio, ([Si] + [Ti] + [Ca] + [Al] + [Sr]) / [Zn]) *2: Number of attached substance on photoreceptor (pieces)
*3: First mixed material *4: Second mixed material *5: Present invention *6: Comparative example

[0167] From the results listed in Table I, it can be seen that the toner of the present invention generates less deposits on the photoreceptor and reduces abrasion of the cleaning blade as compared with the toner of the comparative example. The reason why the number of the toner 16 and the toner 19 attached to the photoreceptor and the abrasion amount of the cleaning blade are good is as follows. This is considered to be because the titanium oxide particles contained in the toner 16 have a high abrasive power, so that the fatty acid metal salt attached to the photoreceptor surface is easily removed. It is also considered that the surface of the photoreceptor is also polished at the same time, so that the photoreceptor layer is greatly worn and the durability is reduced. On the other hand, it is presumed that since the surface of the photoreceptor has a small amount of fatty acid metal salt, the friction coefficient is kept small, the cleaning blade is hardly pulled in, and no photoreceptor deposits are generated. Further, the relationship between the wear of the photoreceptor and the cleaning blade is a trade-off, and it is estimated that the wear amount of the cleaning blade is reduced because the surface of the photoreceptor is easily polished. The toner 19 has a large content and a large liberated amount of calcium titanate. It is thought that the polishing power was increased and it was easier to remove fatty acid metal salts attached to the photoreceptor surface. It is presumed that for the same reason as the toner 16 described above, no photoconductor deposit was generated, and the amount of wear of the cleaning blade was reduced.

Claims

1. An electrostatic image developing toner containing toner particles comprising toner base particles and an external additive,
   wherein a content of titanium oxide as the external additive is 1 part by mass or less based on 100 parts by mass of the toner base particles; and
   an amount of metal [A] (CPS) on a surface of a photoreceptor which is measured by X-ray photoelectron spectroscopy after printing 5,000 sheets at 20% coverage on A4 high-quality paper (basis weight: 68 g/m^2) in an environment of 30 °C and 80 %RH and a photoreceptor wear α value [B] satisfy a relationship of the following expression (1) or expression (2),

$$\text{Expression (1): } 30{,}000 \leq [A] \leq 50{,}000$$

$$\text{Expression (2): } 2.50 \leq [B] \leq 5.00,$$

   wherein that the photoreceptor wear α value [B] is an amount of wear per 100,000 rotations of the photoreceptor.

2. The electrostatic image developing toner described in claim 1,
   wherein the toner particles contain a fatty acid metal salt.

3. The electrostatic image developing toner described in claim 2,
   wherein the fatty acid metal salt is zinc stearate.

4. The electrostatic image developing toner described in claim 3,
   wherein a content of the zinc stearate is in the range of 0.1 to 1.0 part by mass with respect to 100 parts by mass of the toner base particles.

5. The electrostatic image developing toner described in any one of claims 1 to 4,
   wherein in a measurement of an adhesive strength of the external additive to the toner base particles, when amounts of free external additives of Si, Ti, Ca, Al, Sr, and Zn are represented by [Si], [Ti], [Ca], [Al], [Al], [Sr] and [Zn] (unit: kcps), a relationship of the following expression (3) or expression (4) is satisfied,

$$\text{Expression (3): } 0.5 \leq ([Si] + [Ti] + [Ca] + [Al] + [Sr]) / [Zn]) \leq 2.5,$$

$$\text{Expression (4): } 3.5 \leq ([Si] + [Ti] + [Ca] + [Al] + [Sr]) / [Zn]) \leq 8.0.$$

6. The electrostatic image developing toner described in any one of claims 1 to 5,

wherein calcium titanate is contained as the external additive.

7. The electrostatic image developing toner described in claim 6, wherein a content of the calcium titanate is in the range of 0.1 to 1.0 part by mass with respect to 100 parts by mass of the toner base particles.

8. The electrostatic image developing toner described in any one of claims 1 to 7, wherein the toner particles are formed in a split addition of the external additive to the toner base particles.

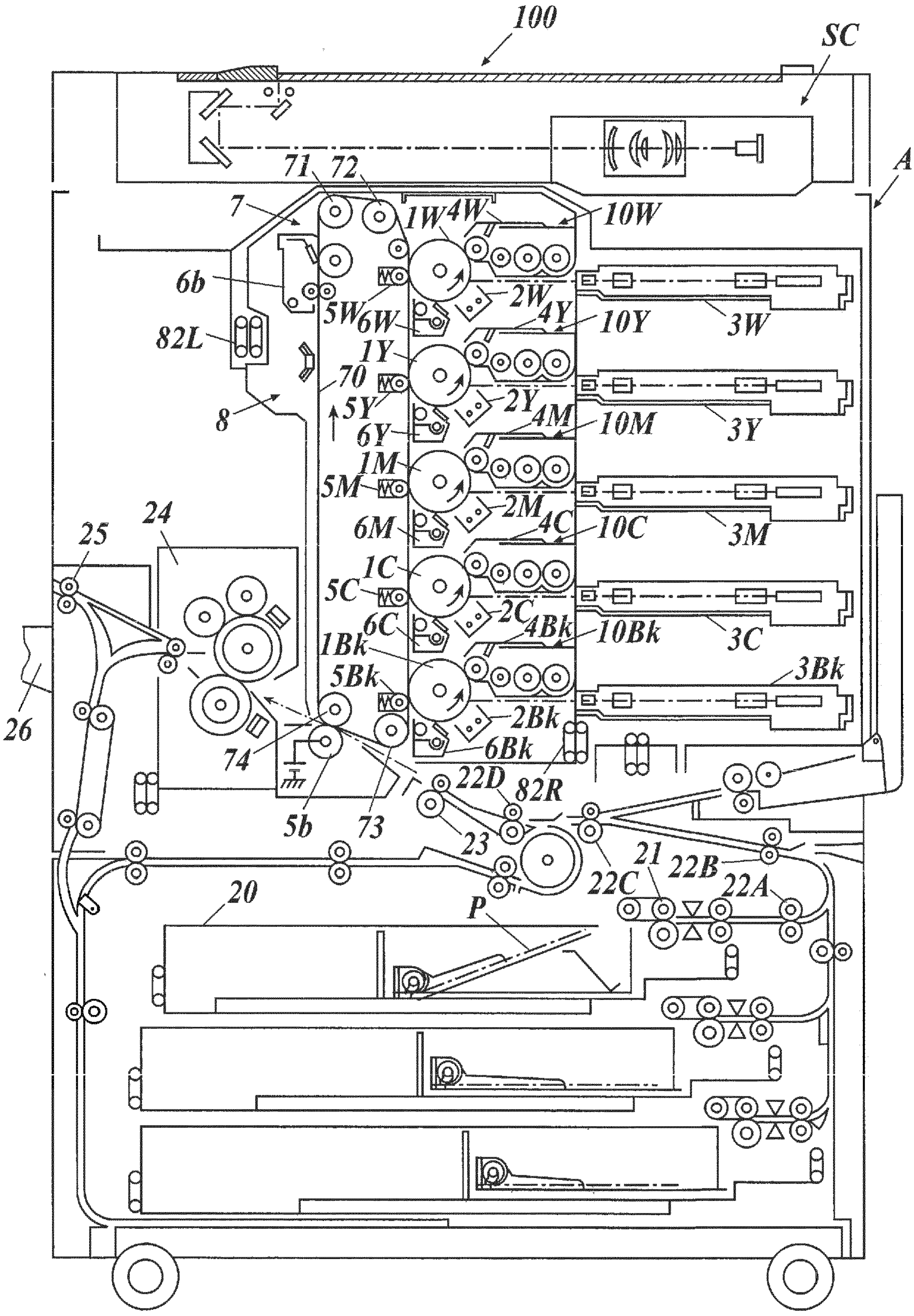
9. A production method of the electrostatic image developing toner described in any one of claims 1 to 8, comprising the step of adding the external additive with a split mixing method to the toner base particles.

10. An image forming method using an electrostatic image developing toner containing toner particles comprising toner base particles and an external additive,
wherein a content of titanium oxide as the external additive is 1 part by mass or less based on 100 parts by mass of the toner base particles; and an amount of metal [A] (CPS) on a surface of a photoreceptor which is measured by X-ray photoelectron spectroscopy after printing 5,000 sheets at 20% coverage on A4 high-quality paper (basis weight: 68 g/m^2) in an environment of 30 °C and 80% RH and a photoreceptor wear α value [B] satisfy a relationship of the following expression (1) or expression (2),

$$\text{Expression (1): } 30{,}000 \leq [A] \leq 50{,}000$$

$$\text{Expression (2): } 2.50 \leq [B] \leq 5.00,$$

wherein the photoreceptor wear α value [B] is an amount of wear per 100,000 rotations of the photoreceptor.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71
72
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6b
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6W
2W
4Y
10Y
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82L
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70
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EUROPEAN SEARCH REPORT

Application Number
EP 20 16 9366

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The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
The Hague	20 August 2020	Vogt, Carola

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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