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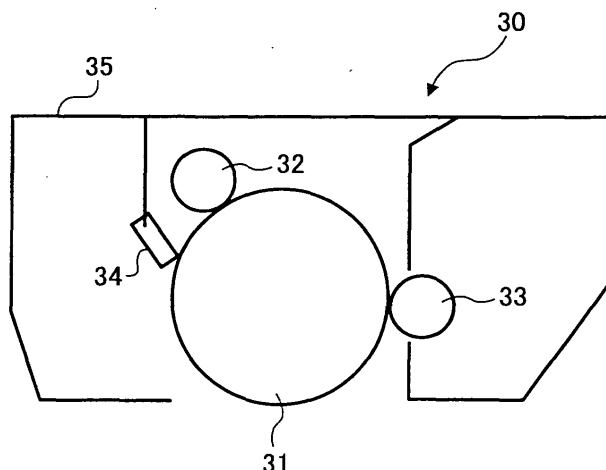
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(54) **Toner, toner container, two-component developer and image forming method and apparatus using the toner**

(57) A toner including a binder resin; and a colorant including an iron oxide compound including Ti in such an amount that the weight of Ti atom is from 10 to 45 % by weight based on the weight of Fe atom therein when measured with a wavelength dispersive fluorescent X-ray analyzer, wherein the content of the black iron oxide compound in the toner is from 15 to 40 % by weight, and the coercive force of the toner is from 2 to 15 kA/m in a magnetic field of 398 Am²/Kg when measured with a

multi-sample rotation type magnetization measurement system from Toei Industry Co., Ltd. A toner container containing the toner. A two-component developer including the toner and a carrier. An image forming method in which a toner image is formed by performing charging; latent image forming; developing using a developer including the toner; image transferring; image fixing; and cleaning. A process cartridge (30) including at least a developing device (33) using the toner and a housing (35).

FIG. 3



Description**BACKGROUND OF THE INVENTION****Field of the Invention**

[0001] The present invention relates to a black color toner for use in image formation. In addition, the present invention relates to a toner container containing the toner, a two component developer including the toner, and an image forming method and an image forming apparatus (such as process cartridge) using the toner.

Discussion of the Background

[0002] Various electrophotographic image forming methods have been disclosed, for example, in US Patent No. 2,297,691, and published examined Japanese Patent Applications Nos. (hereinafter referred to as JP-Bs) 49-23910 and 43-24748.

[0003] In general, electrophotographic image forming methods typically include the following processes:

- (1) an electrostatic latent image is formed on a photosensitive material using one of various methods (latent image forming process);
- (2) the electrostatic latent image is developed with a toner to form a toner image on the photosensitive material (developing process);
- (3) the toner image is transferred to a receiving material such as papers optionally via an intermediate transfer medium (transferring process); and
- (4) the toner image is fixed to the receiving material upon application of heat and/or pressure, resulting in formation of a copy (fixing process).

[0004] The developing methods are broadly classified into wet developing methods in which electrostatic latent images are developed with a liquid developer including a pigment or a dye dispersed in an insulating liquid, and dry developing methods (such as cascade methods, magnetic brush methods and powder cloud methods) in which electrostatic latent images are developed with a dry developer including a toner including a colorant (such as carbon black) dispersed in a resin.

[0005] Recently, in order to prevent environmental pollution and health hazard, a need exists for a toner using safe materials. Therefore, it has been tried to use a powder of black metal compound as a colorant instead of carbon black in view of safety. This is because carbon black, which has been typically used as a black colorant for toners, includes a very small amount of hydrocarbons in which a material such as 3, 4-benzpyrene, which is considered to be a cancer-causing material, is often included.

[0006] Various substitutes for carbon black have been disclosed. For example, published unexamined Japanese Patent Application No. (hereinafter referred to as JP-A) 03-2276 discloses black pigments having a small magnetism, i.e., a polycrystalline black pigment powder including a mixture of Fe_2TiO_5 with a solid solution of $\text{Fe}_2\text{O}_3\text{-TiO}_3$. In addition, JP-As 08-143316 and 2000-10344 have disclosed a black powder having a hematite structure and including Mn.

[0007] The black pigment disclosed in JP-A 03-2276 is prepared by a method in which magnetite is coated with titanium oxide or a method in which a mixture of magnetite with titanium oxide is baked in a non-oxidative atmosphere. Since the black pigment is formed of iron oxide and titanium oxide, which are safe and non-toxic, the black pigment is safe. However, the black pigment has the following drawbacks. When magnetite coated with titanium oxide is baked at a high temperature not lower than 700 °C, hematite is generated and thereby the resultant pigment has a reddish black color, i.e., has a low blackness. Specifically, the L^* value (i.e., lightness) of the black pigment is from 18 to 25, which is lower than that of carbon black. In addition, particles are sintered or united, and therefore it becomes difficult to disperse the pigment so that the pigment achieve a primary particle state.

[0008] The black pigment disclosed in JP-As 08-143316 and 2000-10344 includes a large amount of Mn, which is an environmental pollutant. Therefore, it cannot be said that the black pigment is safe.

[0009] Japanese Patents Nos. 3,101,782, 3,108,823 and 3,174,960 (i.e., JP-As 06-19204, 05-249742 and 05-88412) have proposed to use a magnetic iron oxide including FeO in an amount of from 25 to 30 % by weight as a colorant. This pigment can be used for magnetic toners, but cannot be used for toners for non-magnetic two component developing methods.

[0010] Japanese Patents Nos. 3,224,774 and 3,261,088 (i.e., JP-As 11-157843 and 11-189420) have disclosed magnetite having a residual magnetization not greater than 6 Am²/Kg, and JP-A 2000-319021 discloses a particulate iron oxide which includes Ti in the inner portion of the particles thereof and includes Ti and Fe on the surface portion thereof.

However, these black pigments have a large saturation magnetization of from 80 to 85 Am²/Kg. Therefore, the pigments can be used for magnetic toners, but cannot be used for toners for non-magnetic two component developing methods.

[0011] JP-A 2002-129063 discloses a rutile-form TiO₂ mixture crystal which is coated with Fe₂TiO₄ and which has a saturation magnetization of from 0.5 to 10 Am²/Kg and a particle diameter of from 0.1 to 0.4 μm. In addition, the black pigment has good blackness. However, when a toner including the black pigment is used for recent fixing devices in which toner images are fixed with a thin cylindrical fixing roller while applying a low pressure thereto, the resultant toner images cannot be well fixed on receiving materials. Therefore, the resultant toner images have low blackness.

[0012] JP-A 2002-189313 discloses a toner which includes a metal compound having a saturation magnetization not greater than 30 Am²/Kg and which has a dielectric loss not greater than 50. It is described in the publication that the toner can be used for middle speed fixing devices having a fixing speed of about 180 mm/sec and the resultant fixed toner images have good blackness. However, the toner cannot be well fixed when used for high speed fixing devices having a fixing speed of from 400 to 600 mm/sec, which are needed recently, and thereby the resultant toner images have low blackness.

[0013] JP-A 2002-196528 discloses a toner which includes a metal compound having a saturation magnetization not greater than 40 Am²/Kg in an amount not greater than 20 % by weight. It is described that the resultant toner images have a a* value of from -3.0 to 3.0 and a b* value of from -3.0 to 3.0. However, the toner images having such a* and b* values have a reddish or bluish black color, and it cannot be said that the toner images have good blackness.

[0014] JP-A 2000-10344 discloses a black pigment consisting of a particulate black hematite or a particulate black hydrated iron oxide. This black pigment includes manganese in the core portion, and therefore the black pigment cannot be said to be safe.

[0015] Magnetite is a black pigment including, as a main component, iron oxide which is safe and non-hazardous. However, magnetite has large magnetism. Therefore, particles thereof aggregate and thereby it is hard to uniformly disperse the particles in a toner. In addition, since magnetite is electroconductive, it cannot be used for toners used for two component developing methods and non-magnetic one component developing methods in which toners are required to have an insulation property or a high electric resistance.

[0016] Toner image fixing methods are broadly classified into contact fixing methods and non-contact fixing methods. Specific examples of the contact fixing methods include heat roller fixing methods, belt fixing methods, etc. Specific examples of the non-contact fixing methods include flash fixing methods and oven fixing methods (i.e., atmosphere fixing methods).

[0017] In the heat roller fixing methods, toner images are contacted to a heat roller. Therefore, the fixing methods have good heat efficiency. In addition, a small fixing device can be used therefor. Therefore, the fixing methods are typically used now.

[0018] Recently, in view of energy saving, there is a case where heat sources for fixing devices are put off when a fixing operation is not performed. Such fixing devices are required to rapidly increase the temperature of the heat roller to a predetermined fixing temperature when a fixing operation is desired to start (i.e., a power source is applied). Therefore, the fixing devices typically use a thin fixing roller having a thickness not greater than 1.0 mm for a roller which is to be contacted with toner images, as disclosed in JP-As 2002-82474 and 09-222750. By using such a thin roller, the temperature of the fixing device can be increased very quickly to the predetermined fixing temperature. However, the mechanical strength of the roller decreases, and thereby a high pressure cannot be applied thereto to prevent deformation of the roller. Therefore, the toner used for such fixing devices is needed to have a low temperature fixability much better than those of conventional toners.

[0019] In attempting to solve the problem, several proposals have been made. For example, Japanese Patent No. 2,743,476 (i.e., JP-A 03-2874) discloses a toner for use in the roller fixing methods, which includes a core material including a polyester resin having a specific melt viscosity and a wax having a polar group and a specific melt viscosity, wherein the core material is coated with a resin.

[0020] In addition, JP-As 03-122661 and 04-85550 JP-B 08-16804 have disclosed toners for forming toner images on film receiving materials, which include a polyester resin having a specific melt viscosity (in the temperature range of from 80 °C to 120 °C) and a specific melt viscosity dependence on temperature and a release agent having a specific melt viscosity.

[0021] Further, JP-B 08-12459 discloses a capsule toner for forming toner images on film receiving materials, which include a polyester resin having a specific melt viscosity (in the temperature range of from 80 °C to 120 °C) and a specific melt viscosity dependence on temperature and a release agent having a specific melt viscosity.

[0022] Furthermore, JP-B 07-82250 discloses a toner for forming toner images on film receiving materials, which include a polyester resin having a specific melt viscosity (in the temperature range of from 120 °C to 150 °C) and a specific melt viscosity dependence on temperature, an organic metal compound and a release agent having a specific melt viscosity.

[0023] Furthermore, JP-B 07-72809 discloses a toner which includes a styrene-acrylic resin having a specific melt viscosity dependence on temperature in the range of from 110 °C to 130 °C.

[0024] Furthermore, JP-A 10-246989 discloses a toner which includes a specific charge controlling agent and has a specific melt viscosity curve.

[0025] Recently, there is an increasing need for high quality toner images, and thereby the particle diameter of toner becomes smaller and smaller. When a toner having a small particle diameter is used for image forming, the resultant fixed toner images have poor fixing property because a proper pressure cannot be applied to such a small toner, particularly when the toner is used for the low pressure fixing device mentioned above.

[0026] Because of these reasons, a need exists for a toner which is safe and non-hazardous and which has good charging properties so that high quality images can be produced without causing toner scattering.

SUMMARY OF THE INVENTION

[0027] Accordingly, an object of the present invention is to provide a toner which is safe and non-toxic and which has good charging properties and can produce high quality images even when used for low pressure fixing devices having a thin roller without causing a toner scattering problem.

[0028] Another object of the present invention is to provide a two component developer which can produce high quality images even when used for low pressure fixing devices having a thin roller.

[0029] Yet another object of the present invention is to provide an image forming method and an image forming apparatus (such as process cartridge) by which high quality images can be produced while using a low pressure fixing device having a thin roller.

[0030] Briefly these objects and other objects of the present invention as hereinafter will become more readily apparent can be attained by a toner including a binder resin and a colorant which is an iron oxide compound including Ti in such an amount that the weight of Ti atom is from 10 to 45 % by weight based on the weight of Fe atom therein when measured with a wavelength dispersive fluorescent X-ray analyzer, wherein the content of the black iron oxide compound in the toner is from 15 to 40 % by weight, and the coercive force of the toner is from 2 to 15 kA/m in a magnetic field of 398 Am²/Kg when measured with a multi-sample rotation type magnetization measurement system from Toei Industry Co., Ltd.

[0031] The saturation magnetization σ_s of the toner is preferably from 0.1 to 5.0 Am²/Kg. The true specific gravity of the toner is preferably from 1.35 to 1.55. The volume resistivity of the toner is preferably from 10.9 to 11.4 $\Omega \cdot \text{cm}$ in logarithmic scale.

[0032] The black iron oxide compound is included in an amount of from 21 to 30 % by weight based on total weight of the toner.

[0033] It is preferable that the toner further includes a zirconium compound selected from the group consisting of Zr-containing aromatic oxycarboxylic acids and Zr-containing aromatic oxycarboxylic acid salts.

[0034] It is preferable that when a solid image of the toner having a weight of 0.60 to 0.85 mg/cm² is fixed on an art paper classified into TYPE 1 specified in ISO 12647-2 and the color of the solid image is measured by a method specified in ISO 12647-1 using a colorimeter X-Rite 938 to determine L*, a* and b* of the solid image, the solid image satisfies the following relationships:

$$10 \leq L^* \leq 28, -1.0 \leq a^* \leq 1.0, \text{ and } -1.0 \leq b^* \leq 1.0.$$

[0035] The toner preferably has a weight average particle diameter D₄ of from 3 to 10 μm .

[0036] The black iron oxide compound has an average primary particle diameter of from 0.005 to 1.5 μm , preferably from 0.005 to 1.0 μm and more preferably from 0.005 to 0.5 μm .

[0037] The toner preferably has a melt index (MI) of from 10 to 20 g/min when the melt index is measured by a method specified in JIS K 6760 under conditions of 150 °C in temperature and 2160 g in load.

[0038] The toner preferably has a glass transition temperature (T_g) of from 55 to 65 °C.

[0039] The toner preferably includes a wax. The wax is preferably a carnauba wax, a rice wax or an ester wax, and the content of the wax is preferably from 0.5 to 7 % by weight based on the total weight of the toner.

[0040] It is preferable that tetrahydrofuran(THF)-soluble components of the toner have a molecular weight distribution such that a peak molecular weight M_p is present in a molecular weight range of from 3300 to 5500 when the molecular weight distribution is determined by gel permeation chromatography (GPC).

[0041] As another aspect of the present invention, a toner container containing the toner mentioned above is provided.

[0042] As yet another aspect of the present invention, a two-component developer including a carrier and the toner mentioned above.

[0043] As a further aspect of the present invention, an image forming method is provided which includes the steps:

charging an image bearing member;
 forming an electrostatic latent image on the charged image bearing member;
 developing the electrostatic latent image with a developer including the toner mentioned above to form a toner
 image on the image bearing member;
 5 transferring the toner image on a receiving material;
 fixing the toner image on the receiving material; and
 cleaning a surface of the image bearing member.

[0044] It is preferable that the fixing is performed by passing the receiving material having the toner image thereon
 10 into a pair of rollers, wherein the roller contacting the toner image is a cylinder having a thickness not greater than 1.0
 mm and a pressure (i.e., (load on the rollers) / (contact area)) applied to the pair of rollers is not greater than 1.5×10^5 Pa.

[0045] The toner collected by cleaning the surface of the image bearing member is preferably re-used for the devel-
 oping process.

[0046] The charging is preferably performed using a contact charger (i.e., by contacting a charger to the image
 15 bearing member). The image transferring is preferably performed using a contact transfer member (i.e., by contacting
 a transfer member to the image bearing member with the receiving material therebetween while applying a voltage to
 the contact transfer member).

[0047] As a still further aspect of the present invention, a process cartridge is provided which includes at least a
 20 developing device configured to develop an electrostatic latent image on an image bearing member with a developer
 including the toner mentioned above and a housing. The process cartridge can include one or more of to other devices
 such as a photoreceptor serving as the image bearing member; a charger configured to charge the photoreceptor; and
 a cleaner configured to clean the surface of the photoreceptor.

[0048] These and other objects, features and advantages of the present invention will become apparent upon con-
 sideration of the following description of the preferred embodiments of the present invention taken in conjunction with
 25 the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0049] Various other objects, features and attendant advantages of the present invention will be more fully appreci-
 30 ated as the same becomes better understood from the detailed description when considered in connection with the
 accompanying drawings in which like reference characters designate like corresponding parts throughout and wherein:

FIG. 1 is a schematic view illustrating an image forming apparatus for use in the image forming method of the
 present invention;

35 FIG. 2 is a schematic view illustrating a fixing device for use in the image forming method of the present invention;
 and

FIG. 3 is a schematic view illustrating an embodiment of the process cartridge of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0050] The toner of the present invention includes a binder resin and a colorant which is an iron oxide compound,
 which includes Ti atom in such an amount of from 10 to 45 % by weight based on the weight of Fe atom therein when
 measured with a wavelength dispersive fluorescent X-ray analyzer, wherein the content of the black iron oxide com-
 45 pound in the toner is from 15 to 40 % by weight, and the coercive force of the toner is from 2 to 15 kA/m in a magnetic
 field of $398 \text{ Am}^2/\text{Kg}$ when measured by a multi-sample rotation type magnetization measurement system from Toei
 Industry Co., Ltd.

[0051] The toner has high blackness and can produce high quality images without causing a toner scattering problem
 in image forming apparatus. The toner of the present invention is preferably used for two component developers.

[0052] The toner scattering problem is such that reversely charged toner particles or weakly charged toner particles
 50 on a developing sleeve scatter and thereby the image forming apparatus is contaminated. When the toner has a co-
 ercive force of from 2 to 15 kA/m, and preferably from 5 to 10 kA/m, the toner is properly held by the carrier and the
 developing sleeve used, and thereby occurrence of the toner scattering problem can be prevented even though there
 are reversely charged toner particles or weakly charged toner particles on the developing sleeve. Since the reversely
 or weakly charged toner particles are agitated again in the developing device, the toner is charged so as to have
 55 sufficient charge quantity.

[0053] When the coercive force is too small, the toner scattering problem tends to be caused. In contrast, when the
 coercive force is too large, the toner has poor developing properties, resulting in decrease of image density. This is
 because the attraction between the toner and the carrier used, and between the toner and the developing sleeve used

are too large.

[0054] In the present application, the coercive force is measured by the following method:

- (1) a sample (i.e., a toner) is contained in a container having a diameter of 7 mm and a height of 10 mm;
- (2) the container is set in a magnetization measuring instrument BHU-60 manufactured by Riken Denshi Co., Ltd.;
- (3) the magnetic field is increased from 0 to 398 Am²/Kg to obtain magnetization curve; and
- (4) the coercive force of the sample is determined from the magnetization curve.

[0055] In order that a toner has a coercive force of from 2 KA/m to 15 KA/m, the toner preferably includes a black iron oxide compound, which includes Ti atom in an amount of from 10 to 45 % by weight based on the Fe atom, in an amount of from 15 to 40 % by weight based on the total weight of the toner. In addition, it is preferable that when toner constituents including such a colorant are melted and kneaded to prepare a toner, the kneading is performed while controlling the viscosity of the melted toner constituents so as to be from 10³ to 10⁷ Pa · s (i.e., 10⁴ to 10⁸ poise). This is because the colorant can be uniformly dispersed in the toner constituent mixture and thereby a desirable coercive force can be imparted to the resultant toner.

[0056] Alternatively, it is also preferable that a masterbatch which is prepared by mixing such a black iron oxide compound with a resin including no crosslinked component and has a low molecular weight is mixed with other toner constituents, followed by kneading and pulverizing the mixture.

[0057] In the toner of the present invention, a black iron oxide compound including Ti is used as a colorant. The black iron oxide compound will be explained in detail.

[0058] The black iron oxide compound for use in the toner of the present invention includes Ti in an amount such that the content of Ti atom (hereinafter referred to as the Ti content) is from 10 to 45 % by weight, and preferably from 20 to 40 % by weight, based on the weight of Fe atom.

[0059] When the Ti content is too low, the coercive force of the black iron oxide compound becomes too large, and thereby the developing ability of the resultant toner deteriorates. In contrast, when the Ti content is too high, the coercive force of the black iron oxide compound decreases and in addition the L* value (i.e., lightness) of images produced by the toner increases, resulting in decrease in image density. The L* value is preferably from 10 to 20 and preferably from 10 to 15.

[0060] The Ti content can be determined using a wavelength dispersive fluorescent X-ray analyzer. Specifically, the molar concentrations of Ti and Fe are calculated from the main peaks of Ti and Fe and then a ratio of the molar concentration of Ti to the molar concentration of Fe is determined. In the present application, a wavelength dispersive fluorescent X-ray analyzer RIX 3000 manufactured by RIGAKU CORP. is used to determine the Ti content. The measuring conditions are as follows:

- (1) dispersive crystal: LiF1,
- (2) output power: 50 KV,
- (3) current: 50 mA,
- (4) target: Rh,
- (5) measuring range: 30 mmφ,
- (6) sample holder: aluminum ring having a diameter of 32 mm, and
- (7) sample: pressed in the aluminum ring to be pelletized.

[0061] The black iron oxide compound is preferably a polycrystal powder which includes a solid solution having a structure of Fe₂O₃-FeTiO₃. The black iron oxide compound having such properties has good blackness and small magnetism.

[0062] In addition, the black iron oxide compound preferably has a L* value (i.e., lightness) of from 10 to 20, a a* value of from -1.0 to 1.0, and a b* value of from -1.0 to 1.0. The L*, a* and b* values are the L*, a* and b* of the color gamut diagram defined in CIE 1976.

[0063] The black iron oxide compound preferably has a saturation magnetization not greater than 50.0 Am²/Kg.

[0064] In addition, the black iron oxide compound preferably has an average primary particle diameter of from 0.005 to 1.5 μm, and more preferably from 0.005 to 0.5 μm, so as to be well dispersed in the resultant toner particles and such that the toner have good blackness. In addition, the black iron oxide compound having such an average particle diameter has good thermal conductivity and thereby the resultant toner can be fixed at a relatively low temperature (i.e., the toner has good low temperature fixability).

[0065] When the average primary particle diameter is too small, the kneaded toner constituent mixture becomes too hard, and thereby the toner constituent mixture has poor pulverizability, resulting in deterioration of productivity of the toner. In contrast, when the average primary particle diameter is too large, the thermal conductivity tends to deteriorate (i.e., the toner loses the advantage in low temperature fixability).

[0066] In the present application, the average primary particle diameter is determined by the following method:

- (1) a sample (i.e., a black iron oxide compound) is adhered to a carbon tape;
- (2) coating the sample with Pt-Pd;
- (3) the coated sample is observed and photographed using a scanning electron microscope, H-9000 manufactured by Hitachi Ltd., with 15000 power magnification at an accelerated voltage of 10 KV; and
- (4) the thus obtained particle image is analyzed by an image analyzer, LUZEX, to determine the average primary particle diameter of the sample (i.e., an average of 50 or more particles).

[0067] The method for preparing a black iron oxide compound having such an average primary particle diameter will be explained in detail.

[0068] The black iron oxide compound can be typically prepared by the following method:

- (1) a powder, such as magnetite coated with a titanium compound, a mixture of magnetite with a titanium compound, and hematite coated with a titanium compound, is reduced to prepare a reduced powder;
- (2) the reduced powder is baked at a temperature not lower than 700 °C in a non-oxidative atmosphere; and
- (3) the baked powder is pulverized, resulting in production of the black iron oxide compound.

[0069] When the reduction is performed, it is preferable to use magnetite coated with a titanium compound. This is because the resultant black iron oxide compound has a small magnetism, and thereby a black pigment having a small magnetism can be obtained.

[0070] The shape of the magnetite or hematite for use in manufacturing the black iron oxide compound is not particularly limited, and any magnetite or hematite particles with a shape such as irregular form, spherical form and needle form can be used. The particle diameter of the source material (i.e., magnetite or hematite) is preferably from 0.003 to 1.5 μm.

[0071] The particle diameter of the black iron oxide compound (i.e., the final product) largely depends on the particle diameter of the source material (i.e., magnetite or hematite). Specifically, when a source material having a small particle diameter is used, the resultant black iron oxide compound tends to have a small particle diameter. Namely, by using a source material having a particle diameter of from 0.003 to 1.5 μm, the average primary particle diameter of the resultant black iron oxide compound tends to fall in the range of from 0.005 to 1.5 μm.

[0072] Suitable titanium compounds for use in manufacturing the black iron oxide compound include hydrated titanium oxides, titanium hydroxides, and titanium oxides. When a titanium compound is mixed with a magnetite powder, a water-soluble titanium compound is preferably used.

[0073] Nitrogen gases (N₂ gasses) can be preferably used for producing the non-oxidative atmosphere mentioned above. In an oxidative atmosphere, the desired black iron oxide compound cannot be produced.

[0074] The baking is performed at a temperature not lower than 700 °C. When the temperature is too low, the solid reaction between the iron oxide with a titanium oxide compound cannot be fully induced, and thereby the desired black iron oxide compound cannot be produced.

[0075] The pulverization can be performed using a general pulverizer such as ball mills, attritors, and vibration mills. By using such a pulverizer, a black iron oxide compound having such an average primary particle diameter as mentioned above can be produced.

[0076] In order to produce a black iron oxide compound having an average primary particle diameter of from 0.005 to 1.5 μm, it is preferable that the source material is previously coated with a sintering inhibitor. By coating such a sintering inhibitor, the sintering of the source material can be prevented, and thereby a black iron oxide compound with a desired average primary particle diameter can be produced.

[0077] Suitable sintering inhibitor include compounds including one or more elements selected from the group consisting of Al, Ti, Si, Zr and P. The content of the sintering inhibitor used is preferably from 0.1 to 15 atomic % based on the toner weight of Fe and Ti to obtain good sintering preventing effect, and to prevent the black iron oxide compound from being mixed with the magnetite used as the source material (i.e., to obtain the desired black iron oxide compound having a small magnetism).

[0078] By fixing a black pigment or dye or a blue pigment or dye on the thus prepared black iron oxide compound using a MECHANO MILL (manufactured by Okada Seiko Co., Ltd.) or a MECHANOFUSION SYSTEM (manufactured by Hosokawa Micron Corporation), the blackness of the black iron oxide compound can be further enhanced.

[0079] Specific examples of the black pigments and dyes include iron black, aniline black, graphite, fullerene, etc. Specific examples of the blue pigments and dyes include cobalt blue, Alkali Blue, Victoria Blue lake, phthalocyanine blue, metal-free phthalocyanine blue, partially-chlorinated phthalocyanine blue, Fast Sky Blue, Indanthrene Blue BC, etc. However, the pigments and dyes to be fixed on the black iron oxide compound are not limited thereto.

[0080] The true specific gravity and bulk density of the black iron oxide compound are preferably from 4.0 to 5.0 and

0.5 to 1.2 g/cm, respectively.

[0081] The toner of the present invention preferably has a saturation magnetization σ_s of from 0.1 to 5.0 Am²/Kg to further improve the scattering preventing ability thereof. In this case, the toner has a small magnetism and thereby the toner is held by a developing sleeve, resulting in prevention of the scattering problem. When the saturation magnetization σ_s is too small, the scattering preventing ability is hardly improved. In contrast, when the saturation magnetization σ_s is too large, the developing ability of the toner deteriorates.

[0082] In the present application, the saturation magnetization can be determined by the following method:

- (1) a sample is contained in a cell with an inside diameter of 7 mm and a height of 10 mm of a multi-sample rotation type magnetization measurement system REM-1-10 manufactured by Toei Industry Co., Ltd.; and
- (2) the saturation magnetization of the sample is measured under the following conditions:

magnetic field strength: 398 Am²/Kg

sweep rate: 1 min/hysteresis curve

measuring temperature: 25 °C.

[0083] In order to prepare a toner having a saturation magnetization of from 0.1 to 5.0 Am²/Kg, it is preferable that the toner includes a Ti-containing black iron oxide compound, which includes Ti in an amount such that the content of Ti atom is from 10 to 45 % by weight based on the Fe atom therein, in an amount of from 15 to 40 % by weight based on the total weight of the toner. In addition, it is preferable that the melt viscosity of the toner constituent mixture in the melt-kneading process is preferably controlled so as to be from 10³ to 10⁷ Pa·s (i.e., 10⁴ to 10⁸ poise). In this case, the black iron oxide compound can be uniformly dispersed in the resultant toner particles, and thereby the toner has the desired saturation magnetization. Alternatively, it is preferable to use a method in which the black iron oxide compound is mixed with a resin having a low molecular weight to prepare a masterbatch, and the masterbatch is then melted and kneaded together with other toner constituents, followed by cooling and pulverizing.

[0084] The toner of the present invention preferably has a true specific gravity of from 1.35 to 1.55. In this case, the toner scattering problem can be prevented and occurrence of background development on non-image portions can be also prevented. This is because the difference in specific gravity between a carrier and the toner decreases, and thereby the carrier and the toner can be efficiently agitated, resulting in quick impartment of a desired amount of charge to the toner. It is preferable to use a carrier having a true specific gravity from 1.3 to 2.5 times that of the toner used to effectively impart a desired amount of charge to the toner.

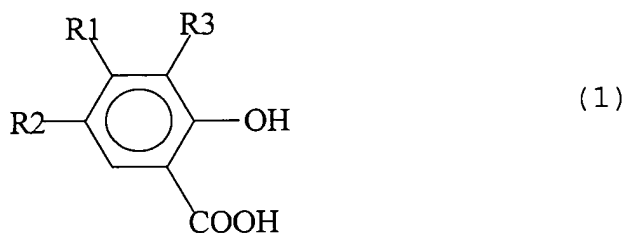
[0085] When the true specific gravity of the toner is too low, the effects mentioned above cannot be produced. In contrast, when the true specific gravity is too high, the developing ability of the toner deteriorates, resulting in decreases in image density of the toner images. In this application, the specific gravity is measured by an air comparison pycnometer, MODEL 930 manufactured by Beckmann Co.

[0086] The volume resistivity of the toner is preferably from 0.9 to 11.4 Ω · cm in logarithmic scale. In this case, the colorant can be well dispersed and thereby the resultant toner has good charge stability, resulting in prevention of occurrence of the toner scattering problem and background development in the non-image areas.

[0087] The content of the black iron oxide compound in the toner of the present invention is preferably not less than 21 % by weight to produce images with high blackness, and not greater than 30 % by weight not to excessively increase the true specific gravity of the toner, i.e., not to deteriorate the developing ability of the toner.

[0088] The toner of the present invention can include a charge controlling agent to control the charge properties thereof. Suitable charge controlling agents include Nigrosine dyes, quaternary ammonium salts, polymers having an amino group, metal-containing azo dyes, complex compounds of salicylic acid, phenolic compounds, zirconium compounds, etc. Among the materials, zirconium compounds such as Zr-containing aromatic oxycarboxylic acids or Zr-containing aromatic oxycarboxylic acid salts are preferably used. By using such a zirconium compound as a charge controlling agent, the resultant toner has good charge rising property and good charge stability.

[0089] Any known aromatic oxycarboxylic acids can be used for the Zr-containing charge controlling agent, but compounds having the following formula (1) are preferably used:

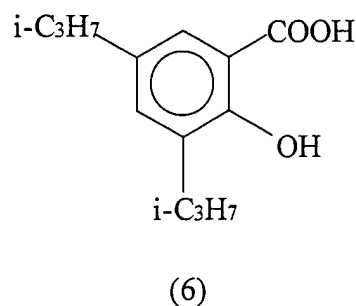
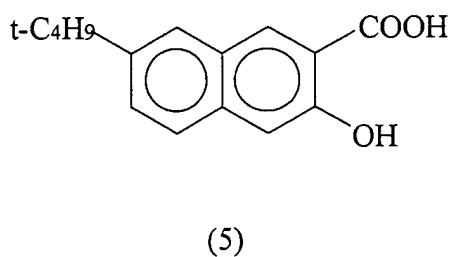
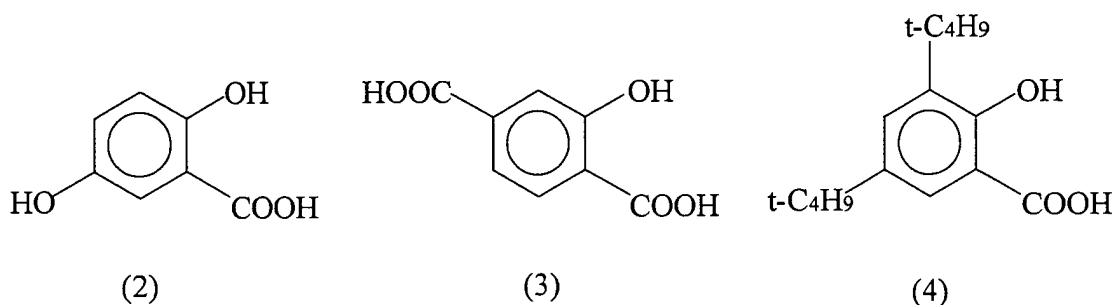


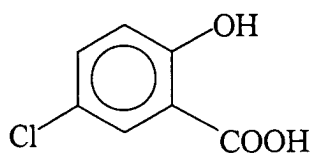
10 wherein R1, R2 and R3 independently represent a hydrogen atom, a halogen atom (e.g., a fluorine atom or a chlorine atom), a hydroxyl group, a carboxyl group, a substituted or unsubstituted alkoxycarbonyl group having from 2 to 11 carbon atoms, a substituted or unsubstituted alkoxy group having from 1 to 10 carbon atoms, a substituted or unsubstituted alkyl group having from 1 to 10 carbon atoms, a substituted or unsubstituted alkenyl group having from 1 to 10 carbon atoms, or a substituted or unsubstituted aryl group having from 6 to 18 carbon atoms, and R1 and R2 or R1 and R3 optionally share a bond connectivity to form a ring.

15 **[0090]** Specific examples of the substituted or unsubstituted alkyl group having from 1 to 10 carbon atoms include a methyl group, an ethyl group, a propyl group, and a butyl group. Specific examples of the substituted or unsubstituted aryl group include a phenyl group.

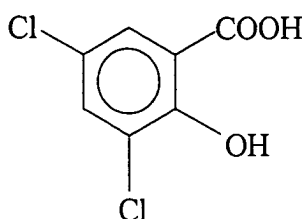
20 **[0091]** Among these groups, a hydrogen atom, a chlorine atom, a hydroxyl group, a carboxyl group, and an alkyl group having from 1 to 10 carbon atoms are preferable.

[0092] Specific examples of the preferable aromatic oxycarboxylic acids include compounds having one of the following formulae (2) to (9):

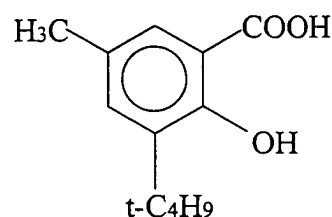




(7)



(8)



(9)

These Zr-containing charge controlling agent can impart good charging properties to the toner.

[0093] Since the toner of the present invention includes a Ti-containing black iron oxide compound, which has good thermal conductivity because Ti has good thermal conductivity, the toner has good low temperature fixability. Therefore, even when the toner is used for high speed image forming apparatus, the resultant toner images have good fixing property.

[0094] When the lightness and color tone of a black toner are represented by a L^* - a^* - b^* color system, the toner of the present invention preferably has L^* , a^* and b^* values of from 10 to 28, -1.0 to 1.0 and -1.0 to 1.0, respectively, and more preferably from 10 to 20, -0.5 to 0.5 and -0.5 to 0.5, respectively. The value L^* is even more preferably from 10 to 15. The method for measuring the L^* , a^* and b^* values are as follows:

(1) a solid image of a toner having a weight of from 0.60 to 0.85 mg/cm² is formed and fixed on an art paper classified into TYPE 1 specified in ISO 12647-2; and

(2) the L^* , a^* and b^* values of the solid image are measured by a method specified in ISO 12647-1 using a colorimeter X-Rite 938, wherein a light source D50 is used and the viewing angle is 2°.

[0095] When the toner satisfies these conditions, the resultant toner images have blackness and color tone as good as those of the conventional toners using carbon black as a colorant. When the L^* , a^* and b^* values fall out of the ranges, the toner images have a reddish or yellowish black color tone, namely, the toner images have poor blackness.

[0096] In this regard, the value L^* means a ratio $L1/L0$, wherein $L0$ represents the total light quantity of light irradiating the toner image and $L1$ represents the total light quantity of the light reflected from the toner image. The value a^* represents whether the toner image has a reddish or greenish color tone, and the value b^* represents whether the toner image has a yellowish or bluish color tone. When the value L^* is small, the toner images have a color tone near the true black color. When the value a^* is large ($a^* > 1.0$), the toner images have a reddish black color. In contrast, when the value a^* is small ($a^* < -1.0$), the toner images have a greenish black color. In addition, when the value b^* is large ($b^* > 1.0$), the toner images have a yellowish black color. In contrast, when the value b^* is small ($b^* < -1.0$), the toner images have a bluish black color.

[0097] The specifications of the art paper of TYPE 1 specified in ISO 12647-2 are as follows:

L^* : 93 ± 3
 a^* : 0 ± 2
 b^* : -3 ± 2
 glossiness: 65 ± 5 (%)

[0098] The data for the art paper used for evaluating the toner of the present invention are as follows.

L^* : 93
 a^* : 0.3
 b^* : 0.2
 glossiness: 65 (%)

[0099] In order to prepare a toner satisfying the conditions mentioned above, it is preferable to use a polyester resin as a binder resin. In this case, the resultant toner has a good low temperature fixability and high glossiness. Among polyester resins, polyester resins including tetrahydrofuran-insoluble components in an amount of from 5 to 25 % are preferable. When such polyester resins are used, the black iron oxide compound can be well dispersed due to increase

of the torque in the kneading process, and thereby the resultant toner has the desired values L^* , a^* and b^* .

[0100] In addition, it is also preferable that a polyester resin including no tetrahydrofuran-insoluble component is mixed and kneaded with the black iron oxide compound in a ratio of from 1/1 to 2/1 using a two roll mill or the like to prepare a masterbatch and the masterbatch is then mixed with other toner constituents, followed by pulverizing, to prepare a toner.

[0101] The toner of the present invention preferably has a melt viscosity such that the melt index (MI) thereof is from 10 to 20 g/min when measured at 150 °C while applying a load of 2160 g to the toner. The toner having such a melt index has good low temperature fixability. In addition, the black iron oxide compound can be well dispersed, the toner also has high blackness. Particularly, this toner is preferably used for high speed image forming apparatus and image forming apparatus having a low pressure fixing device in which a low pressure is applied to the fixing roller. When the melt index is too small, the low temperature fixability of the resultant tone is unsatisfactory. In contrast, when the melt index is too large, the hot offset resistance of the toner tends to deteriorate.

[0102] Further, it is preferable that when the tetrahydrofuran-soluble components of the toner are subjected to gel permeation chromatography (GPC) to determine the molecular weight distribution of the toner, the peak molecular weight M_p is observed in a range of from 3300 to 5500. In this case, the toner has good low temperature fixability as well as the desired values L^* , a^* and b^* .

[0103] When the peak molecular weight is too low, the toner particles tend to be fused in the pulverization process, resulting in formation of aggregated particles. In contrast, when the peak molecular weight is too high, good low temperature fixability cannot be imparted to the resultant toner.

[0104] In order that the toner has such a melt index and a peak molecular weight as mentioned above, it is preferable to use a resin having a peak molecular weight M_p of from 3300 to 7000 and including tetrahydrofuran-insoluble components in an amount of from 5 to 25 % by weight as a binder resin. In addition, in order to improve the low temperature fixability of the toner, it is preferable to add a resin including no tetrahydrofuran-insoluble components.

[0105] The toner of the present invention preferably has a glass transition temperature of from 55 to 65 °C to have a good combination of low temperature fixability and preservability. In the present application, the glass transition temperature (T_g) is measured by the following method based on ASTM D3418-82 incorporated herein by reference.

- (1) a sample having a weight of from about 5 to 10 mg is precisely weighed;
- (2) the sample is contained in an aluminum pan of a differential scanning calorimeter, DSC-7 from Perkin-Elmer, while a reference sample (e.g., aluminum oxide) is also contained in an aluminum pan;
- (3) the sample and reference sample are heated from 30 to 200 °C at a temperature rising speed of 10 °C/min, followed by cooling to room temperature; and
- (4) the sample and the reference sample are heated again from 30 to 200 °C at a temperature rising speed of 10 °C/min to obtain a DTA curve (i.e., an endothermic peak) in a range of from 40 to 100 °C.

[0106] The melt index is measured by a method based on JIS K7210 using an instrument, FLOW RATE COUNTER TYPE C-5059D from Toyo Seiki Seisaku-sho, Ltd. The measuring conditions are as follows:

Load: 2160 g
 Measuring temperature: 150 °C
 Weight of sample: 5 g

[0107] The peak molecular weight M_p is determined by gel permeation chromatography using a mono-dispersion polystyrene as a reference. The measuring conditions are as follows.

Detector: SHODEX RI-71S
 Solvent: tetrahydrofuran
 Column: KF-G, Kf-807LX3 and KF800D
 Flow rate: 1.0 ml/min
 Sample: 0.25 % tetrahydrofuran solution

[0108] The toner of the present invention preferably has a weight average particle diameter (D_4) of from 3 to 10 μm . In this case, the toner has a good combination of low temperature fixability and blackness because the toner has good heat conductivity and the recessed portions of receiving materials can be filled with the toner particles. When the weight average particle diameter is too small, the toner particles tend to scatter. Therefore, there is a possibility that operators breathe in the toner particles, which is not preferable in view of safety. In contrast, when the weight average particle diameter is too large, the heat conductivity of the toner deteriorates, resulting in deterioration of low temperature fixability.

[0109] The average particle diameter and particle diameter distribution of toner particles can be measured, for example, with an instrument such as COULTER COUNTER TA-II or MULTISIZER II manufactured by Coulter Electronics, Inc. The procedure is as follows:

- (1) a surfactant serving as a dispersant, preferably 0.1 to 5 ml of a 1 % aqueous solution of an alkylbenzenesulfonic acid salt, is added to an electrolyte such as 1 % aqueous solution of first class NaCl or ISOTON-II manufactured by Coulter Electronics, Inc.;
- (2) 2 to 20 mg of a sample (a toner or toner particles) to be measured is added into the mixture;
- (3) the mixture is subjected to an ultrasonic dispersion treatment for about 1 to 3 minutes; and
- (4) the particle diameter distribution curves (on a volume basis and a number basis) of the sample are obtained using the instrument and an aperture of 100 μm ; and
- (5) the weight average particle diameter (D4) and the number average particle diameter (D1) are determined from the particle diameter distribution curves.

[0110] The particle diameter channels are following 13 channels:

- $$2.00 \mu\text{m} \leq C1 < 2.52 \mu\text{m}; 2.52 \mu\text{m} \leq C2 < 3.17 \mu\text{m};$$
- $$3.17 \mu\text{m} \leq C3 < 4.00 \mu\text{m}; 4.00 \mu\text{m} \leq C4 < 5.04 \mu\text{m};$$
- $$5.04 \mu\text{m} \leq C5 < 6.35 \mu\text{m}; 6.35 \mu\text{m} \leq C6 < 8.00 \mu\text{m};$$
- $$8.00 \mu\text{m} \leq C7 < 10.08 \mu\text{m}; 10.08 \mu\text{m} \leq C8 < 12.70 \mu\text{m};$$
- $$12.70 \mu\text{m} \leq C9 < 16.00 \mu\text{m}; 16.00 \mu\text{m} \leq C10 < 20.20 \mu\text{m};$$
- $$20.20 \mu\text{m} \leq C11 < 25.40 \mu\text{m}; 25.40 \mu\text{m} \leq C12 < 32.00 \mu\text{m}; \text{ and}$$
- $$32.00 \mu\text{m} \leq C13 < 40.30 \mu\text{m}.$$

[0111] Thus, particles having a particle diameter not less than 2.00 μm and less than 40.30 μm are targeted.

[0112] The toner of the present invention can include a wax. Suitable waxes for use in the toner include carnauba waxes, rice waxes, and ester waxes. The content of the wax in the toner is preferably from 0.5 to 7 % by weight based on the total weight of the toner, to impart good offset resistance to the toner.

[0113] The toner of the present invention includes a binder resin. Known resins for use as binder resins in conventional toners can be used for the toner of the present invention.

[0114] Specific examples of the resins include styrene resins (homopolymers or copolymers obtained from styrene monomer and/or substituted styrene compounds) such as polystyrene, poly- α -methylstyrene, styrene - chlorostyrene copolymers, styrene - propylene copolymers, styrene - butadiene copolymers, styrene - vinyl chloride copolymers, styrene - vinyl acetate copolymers, styrene - maleic acid copolymers, and styrene - acrylate copolymers, styrene - methacrylate copolymers, styrene - methyl α -chloroacrylate copolymers, styrene - acrylonitrile - acrylate copolymers; polyester resins; epoxy resins; vinyl chloride resins; rosin-modified maleic acid resins; phenolic resins; polyethylene resins; polypropylene resins; petroleum resins; polyurethane resins; ketone resins; ethylene - ethyl acrylate copolymers; xylene resins; polyvinyl butyral resins; etc.

[0115] These resins can be used alone or in combination. The method for manufacturing the resins is not particularly limited and any known polymerization methods such as bulk polymerization methods, solution polymerization methods, emulsion polymerization methods and suspension polymerization methods can be used.

[0116] Among the resins, polyester resins are preferably used because good low temperature fixability can be imparted to the resultant toner.

[0117] Polyester resins are prepared by subjecting an alcohol and a carboxylic acid to a polycondensation reaction.

[0118] Specific examples of the alcohol include glycols such as ethylene glycol, diethylene glycol, triethylene glycol, and propylene glycol; bisphenols such as 1,4-bis (hydroxymethyl) cyclohexane, and bisphenol A; alcohols having two hydroxyl groups; and polyhydric alcohols having three or more hydroxyl groups.

[0119] Specific examples of the carboxylic acids include dibasic organic acids such as maleic acid, fumaric acid, phthalic acid, isophthalic acid, terephthalic acid, succinic acid, and malonic acid; polybasic carboxylic acids having three or more carboxyl groups, such as 1,2,4-benzenetricarboxylic acid, 1,2,5-benzenetricarboxylic acid, 1,2,4-naphthalenetetracarboxylic acid, 1,2,5-hexanetricarboxylic acid, 1,3-dicarboxyl-2-methylenecarboxypropane, and 1,2,7,8-octanetetracarboxylic acid.

[0120] Polyester resins having a glass transition temperature of from 55 to 70 $^{\circ}\text{C}$ can be preferably used as the binder resin of the toner of the present invention.

[0121] The toner of the present invention optionally includes additives (external additives) such as fluidity improving agents. Suitable materials for use as the additive include silica, aluminum oxide and titanium oxide. When an additive is added to improve the fluidity of the toner, it is preferable to use hydrophobized silica and hydrophobized rutile titanium oxide, which have an average particle diameter of from 0.001 to 1 μm , and preferably from 0.005 to 0.1 μm . Particularly,

silica and titania which are treated with an organic silane compound are preferably used. The content of such an additive in the toner is generally from 0.1 to 5 % by weight, and preferably from 0.2 to 2 % by weight, based on the total weight of the toner.

[0122] Then the method for manufacturing the toner of the present invention will be explained. In order to manufacture the toner of the present invention, known toner manufacturing methods including the following processes can be used:

- (1) toner constituents including a binder resin, a charge controlling agent, and a colorant are mechanically mixed (mixing process);
- (2) the toner constituent mixture is melted and kneaded (kneading process);
- (3) after cooled, the kneaded mixture is pulverized (pulverization process); and
- (4) the pulverized toner constituent mixture is classified (classification process).

[0123] The particles (hereinafter referred to as by-product) which are produced in the pulverization and classification processes and which have a diameter out of the predetermined range can be returned to the mixing or kneading process to be reused. In this regard, the weight ratio (B/C) of the by-product (B) to new toner constituents (C) is from 1/99 to 50/50.

[0124] In the mixing process, toner constituents such as binder resins, charge controlling agents and colorants (optionally by-product) are mechanically mixed, for example, using a mixer having a rotating blade.

[0125] In the kneading process, the toner constituent mixture is melted and kneaded using a kneader such as continuous kneaders (e.g., uniaxial continuous kneaders, and biaxial continuous kneaders), and batch kneaders such as roll mills. In this regard, it is important to perform the kneading process under such conditions as not to cut the molecular chains of the binder resin used. Specifically, the kneading temperature is preferably set so as not to be far from the melting point of the binder resin used. Namely, when the kneading temperature is much lower than the melting point of the binder resin, the molecular chain of the binder resin is cut. In contrast, when the kneading temperature is much higher than the melting point, the colorant cannot be well dispersed.

[0126] In the pulverization process, the kneaded mixture is pulverized. It is preferably to at first crush the kneaded mixture and then pulverize the crushed toner constituent mixture. In this case, it is preferable to use a method in which the crushed toner constituent mixture is fed by jet air so as to collide against a collision plate, or a method in which the crushed toner constituent mixture is fed to a narrow gap between a rotor and a stator.

[0127] When the pulverization operation is completed, the resultant powder is classified by applying a centrifugal force thereto to obtain a toner having a desired particle diameter.

[0128] Alternatively, toner particles can be prepared by another method such as spray drying methods, suspension polymerization methods in which a suspension including a colorant and a monomer is polymerized, emulsion polymerization methods in which particles are prepared by an emulsion polymerization are aggregated and solution dispersing methods in which a toner constituent mixture solution or dispersion of an organic solvent is dispersed in an aqueous medium, followed by evaporation of the organic solvent.

[0129] The thus prepared toner particles can be mixed with an external additive, such as particulate inorganic materials (e.g., hydrophobized silica and titania), to improve the fluidity, preservability, developing property and transferring property.

[0130] An external additive can be mixed with toner particles using a known mixer for powders. In this regard, it is preferable to use a mixer which is equipped with a jacket such that the temperature of the mixing vessel can be controlled. In order to apply a proper stress to the external additive and the toner particles, the following methods can be used:

- (1) the external additive is gradually added to the toner particles;
- (2) the rotation speed, mixing time and mixing temperature are properly controlled; or
- (3) at first a strong stress is applied, followed by application of weak stress, or vice versa.

[0131] Suitable mixers for use in the external additive mixing process include V-form mixers, rocking mixers, Loedge Mixer, Nauter Mixer, Henschel Mixer, etc.

[0132] The toner of the present invention can be mixed with a carrier so as to be used as a two component developer. Suitable materials for use as the carrier include glass, iron, ferrite, nickel, zircon, silica or the like materials. The carrier preferably has a particle diameter of from 30 to 1000 μm , and more preferably from 30 to 80 μm , to impart a proper amount of charge to the toner. The carrier can be coated with a resin. Specific examples of the resin include styrene-acrylic copolymers, silicone resins, polyamide resins, polyvinylidene fluoride resins, etc.

[0133] The thus prepared developer can be mixed with an external additive, such as particulate inorganic materials (e.g., hydrophobized silica and titania), to improve the fluidity, preservability, developing property and transferring property.

[0134] An external additive can be mixed with the developer using a known mixer for powders. In this regard, it is preferable to use a mixer which is equipped with a jacket such that the temperature of the mixing vessel can be controlled. In order to apply a proper stress to the external additive and the toner particles, the following methods can be used:

- (1) the external additive is gradually added to the toner particles;
- (2) the rotation speed, mixing time and mixing temperature are properly controlled; or
- (3) at first a strong stress is applied, followed by application of weak stress, or vice versa.

[0135] Suitable mixers for use in the external additive mixing process include V-form mixers, rocking mixers, Loedge Mixer, Nauter Mixer, Henschel Mixer, etc.

[0136] The toner of the present invention is contained in a toner container when used. In general, such a toner container is delivered to users and the users set the toner container in their image forming apparatus. The shape of the toner container is not particularly limited, and for example, known containers such as bottles, cartridges and volume-reducing flexible cartridges can be used as the toner container.

[0137] The image forming method of the present invention is not particularly limited, and any known image forming methods using electrophotography and a dry toner can be used. The image forming method of the present invention can be used for any image forming apparatus such as copiers and printers using an image forming methods such as electrophotography, electrostatic recording and the like.

[0138] Then the image forming method of the present invention will be explained in detail referring to drawings.

[0139] FIG. 1 is a schematic view illustrating an image forming apparatus (i.e., a digital copier) for use in the image forming method of the present invention.

[0140] Numeral 100 denotes the image forming apparatus. The image forming apparatus 100 includes a drum-form photoreceptor 1 serving as an image bearing member. Around the photoreceptor 1, a charger 2; a light irradiator 3; a developing device 4; a transfer device 5; a cleaner 6; a recycling device 19; and a fixing device 10, are arranged in a rotation direction of the photoreceptor 1 indicated by an arrow A.

[0141] The image of an original set on an original table 7 is read by an image reading device 8. The light irradiator 3 irradiates the photoreceptor 1, which is previously charged with the charger 2, with imagewise light corresponding to the original image to form an electrostatic latent image on the photoreceptor 1. The developing device 4 develops the electrostatic latent image with a developer including the toner of the present invention to form a toner image on the photoreceptor 1. The transfer device 5 electrostatically transfers the toner image on a receiving material, which is timely fed from a paper tray by a paper feeding device 9. The toner image is fixed on the receiving material by the fixing device 10, resulting in formation of a copy. The copy is discharged from the main body of the image forming apparatus 100.

[0142] On the other hand, toner particles remaining on the surface of the photoreceptor 1 even after the image transfer process are removed by the cleaner 6. The toner particles collected by the cleaner 6 are returned by the recycling device 19 to a hopper of the developing device 4. The recycled toner is mixed with the replenished toner to be reused for developing.

[0143] Currently, contact chargers (such as charging rollers and charging blades), contact transfer devices (such as transfer belts) and contact cleaners (such as cleaning blades) are used to reduce the amount of ozone generated. When using these contact devices, a problem in that toner particles are fixed to the contact members tends to occur. Since the toner of the present invention includes a fine metal compound (i.e., the black iron oxide compound) which has a proper abrading property, occurrence of such a problem can be prevented.

[0144] In recycling systems, toner particles tend to be aggregated due to pressure applied to the toner particles in the recycling passage. Since the fine metal compound has a proper hardness, occurrence of aggregation of the recycled toner particles can be prevented.

[0145] When the above-mentioned contact devices are used, it is preferable to use an electroconductive rubber for the contact elements.

[0146] The fixing device 10 has a structure such that a receiving material bearing a toner image thereon is passed through a nip portion between a pair of rollers to fix the toner image upon application of heat thereto. It is preferable that the thickness of one of the pair of rollers, which contacts toner images, is not greater than 1.0 mm and the pressure ((load on the rollers) / (contact area)) applied to the pair of rollers is not greater than 1.5×10^5 Pa.

[0147] An embodiment of the fixing device is illustrated in FIG. 2. Numerals 21 and 22 denote a fixing roller and a pressure roller, respectively. The fixing roller 21 includes a metal cylinder 23 which is typically made of a heat conductive metal such as aluminum, iron, stainless steel and brass, and an offset preventing layer 24 which is formed on the metal cylinder 23 and which is typically made of a material such as RTVs (room temperature vulcanizing rubbers), silicone rubbers, PFA (i.e., tetrafluoroethylene - perfluoroalkylvinyl ether copolymers), and PTFE (i.e., polytetrafluoroethylene). In addition, a heater 25 (such as lamps) is arranged in the fixing roller 21.

[0148] The pressure roller 22 has a structure similar to that of the fixing roller 21. Namely, the pressure roller 22 has a metal cylinder 26, an offset preventing layer 27 (typically made of PFA or PTFE) and a heater 28 which is optionally arranged in the metal cylinder 26.

[0149] The fixing roller 21 and the pressure roller 22 are rotated while being pressed to each other using a spring (not shown). A receiving material S bearing a toner image T is fed so as to pass through the nip between the fixing roller 21 and the pressure roller 22. Thus, the toner image T is fixed on the receiving material S.

[0150] Since the metal cylinder 23 of the fixing roller 21 is so thin as not greater than 1.0 mm, the fixing roller 21 has good temperature rising property, namely, the temperature of the fixing roller 21 can be rapidly increased to the desired fixing temperature. The thickness of the metal cylinder 23 is preferably from 0.2 to 0.7 mm.

[0151] As mentioned above, the pressure applied to the fixing roller 21 and the pressure roller 22 is preferably not greater than 1.5×10^5 Pa. The pressure (P) is defined as the following equation:

$$P = L/CA,$$

wherein L represents load applied to both ends of the rollers, and CA represents the contact area of the rollers.

[0152] The contact area can be determined as follows.

(1) a sheet which can change its surface property upon application of heat thereto, such as OHP (overhead projection) sheets, is fed into the nip between the fixing roller and the pressure roller, which are heated to the fixing temperature;

(2) feeding of the sheet is suddenly stopped so that the sheet is sandwiched by the rollers;

(3) tens second after stopping the sheet, the sheet is fed again to be discharged; and

(4) the area of the portion of the sheet, whose surface condition is changed, is measured to determine the contact area.

[0153] With respect to the pressure, the higher the pressure, the better fixing property the fixed toner has. However, when the pressure is increased, the thin metal cylinder of the fixing roller tends to be deformed. Therefore, the pressure is preferably not greater than 1.5×10^5 Pa, and more preferably from 0.5 to 1.0×10^5 Pa.

[0154] Since the toner of the present invention has good heat conductivity, toner images can be securely fixed on receiving materials even when the roller pressure is relatively low. Therefore, the resultant toner images have good blackness.

[0155] The process cartridge of the present invention includes at least a developing device configured to develop electrostatic latent images with the toner of the present invention and a housing, and optionally includes one or more devices selected from photoreceptors, chargers, and cleaners.

[0156] FIG. 3 is a schematic view illustrating an embodiment of the process cartridge of the present invention.

[0157] Numeral 30 denotes the process cartridge. The process cartridge 30 includes a photoreceptor 31, a charger 32, a developing device 33, a cleaner 34 and a housing 35.

[0158] The process cartridge 30 can be detachably set in an image forming apparatus such as copiers and printers.

[0159] The image forming apparatus including such a process cartridge can perform image forming operations similar to those mentioned above (i.e., charging, irradiating, developing, transferring, fixing, cleaning, etc.).

[0160] Having generally described this invention, further understanding can be obtained by reference to certain specific examples which are provided herein for the purpose of illustration only and are not intended to be limiting. In the descriptions in the following examples, the numbers represent weight ratios in parts, unless otherwise specified.

EXAMPLES

Manufacturing Example of black iron oxide compound

Manufacturing Example 1 to 4

[0161] A particulate hematite and a titanium oxide were baked under a nitrogen gas flow. The content of Ti and the other baking conditions are described in Table 1. Then the baked hematite was pulverized using a ball mill.

[0162] Thus, black iron oxide compounds Nos. 1 to 4 were prepared.

Manufacturing Example 5 to 12

[0163] A particulate hematite, which had been coated with a titanium hydroxide, was reduced to prepare a reduced

hematite. Then the reduced hematite was baked under a nitrogen gas flow. The content of Ti and the other baking conditions are described in Table 1. Then the baked hematite was pulverized using a ball mill. A metal-free phthalocyanine blue pigment was fixed on the surface of the thus pulverized hematite using a MECHANOFUSION SYSTEM (manufactured by Hosokawa Micron Corp.). This operation was performed at 600 °C.

[0164] Thus, black iron oxide compounds Nos. 5 to 12 were prepared.

Table 1

Black iron oxide compound	Ti content (% by weight)	Baking temperature (°C)	Baking time (minute)	Average primary particle diameter (μm)
No. 1	10	800	120	0.003
No. 2	45	1000	100	1.7
No. 3	30	900	120	0.002
No. 4	20	900	110	0.04
No. 5	25	850	110	0.005
No. 6	15	950	100	0.10
No. 7	30	760	120	0.8
No. 8	15	880	120	1.2
No. 9	11	900	100	0.090
No. 10	5	900	100	0.12
No. 11	55	880	100	1.5
No. 12	58	850	120	0.07

[0165] The Ti content was determined by the wavelength dispersive fluorescent X-ray analysis mentioned above.

[0166] The average primary particle diameter was determined by the above-mentioned measuring method using a transmission electron microscope H-9000 from Hitachi Ltd.

Example 1

[0167] The following components were mixed.

Styrene-n-butyl acrylate copolymer (THF-insoluble component content of 30 %; Tg of 72 °C)	58 parts
Black iron oxide compound No. 1	35 parts
Carnauba wax	5 parts
Charge controlling agent (chromium-including azo dye TRH-1 from Hodogaya Chemical Co., Ltd.)	2 parts

[0168] The mixture was kneaded for 10 minutes at 160 °C using a biaxial extruder. After being cooled, the kneaded mixture was pulverized and classified. Thus, toner particles having a weight average particle diameter of 10.5 μm, which was determined by the method mentioned above, were prepared. Then 0.5 parts of a silica powder R-972 from Clariant Japan K. K. were mixed with 100 parts of the toner particles using a Henschel mixer.

[0169] Thus, a toner of Example 1 was prepared.

[0170] The toner was evaluated by the following methods.

1. Magnetic properties

[0171] A sample was contained in a cell with an inside diameter of 7 mm and a height of 10 mm of a multi-sample rotation type magnetization measurement system REM-1-10 manufactured by Toei Industry Co., Ltd. to obtain a hysteresis curve. The saturation magnetization σ_s and coercive force H of the sample were determined from the hysteresis curve. The measurements were performed under the following conditions:

magnetic field strength: 398 Am²/Kg
sweep rate: 1 min/hysteresis curve
measuring temperature: 25 °C

2. Glass transition temperature (T_g)

[0172] The glass transition temperature of the toner was determined by the method as mentioned above using an instrument DSC-7 from Perkin-Elmer.

3. Melt index (MI)

[0173] The melt index of the toner was measured by the method as mentioned above using an instrument, FLOW RATE COUNTER TYPE C-5059D from Toyo Seiki Seisaku-sho, Ltd.

4. Peak molecular weight (M_p)

[0174] The molecular weight distribution of the tetrahydrofuran(THF)-soluble components of the toner was determined by gel permeation chromatography to determine the peak molecular weight thereof. The measuring method is mentioned above.

5. Minimum fixable temperature (MFT)

[0175] The toner was mixed with a carrier, which had been prepared by coating a particulate ferrite having an average particle diameter of 50 μm with a silicone resin, at a toner concentration of 4.0 % by weight. Thus, a developer was prepared.

[0176] The developer was set in a copier IMAGIO MF6550 which had been modified such that the fixing device is replaced with a fixer having such a structure as illustrated in FIG. 2 to produce copies including a solid image. In this case, fixing was performed while the pressure applied to the fixing roller 21 was controlled so as to be 0.7 x 10⁵ Pa, and the fixing temperature was changed by changing the temperature of the heater 25.

[0177] At first, the image density (ID₁) of an area of the solid image was measured with a MACBETH densitometer. Then an adhesive tape (SCOTCH MENDING TAPE from Sumitomo 3M Ltd.) was attached to the area of the solid image while applying a predetermined pressure thereto. The adhesive tape was slowly peeled from the solid image. Then the image density (ID₂) of the area of the solid image from which the adhesive tape was peeled was measured with the densitometer to determine the fixing rate (i.e., (ID₂/ID₁) x 100). The fixing temperature above which the fixing rate is not less than 80 % is defined as the minimum fixable temperature.

[0178] IMGIO MF6550 uses a transfer belt, a charging roller and a toner recycling system.

6. Hot offset temperature (HOT)

[0179] The toner was set in a copier IMAGIO MF6550 which had been modified such that the fixing device is replaced with a fixer having such a structure as illustrated in FIG. 2 to produce copies. In this case, fixing was performed while the pressure applied to the fixing roller 21 was controlled so as to be 0.7 x 10⁵ Pa, and the fixing temperature was changed by changing the temperature of the heater 25.

[0180] The copy images were visually observed to determine whether the fixed images have a hot offset problem. The hot offset temperature is defined as the fixing temperature above which the hot offset problem is caused.

7. Image qualities

(1) Image density

[0181] A running test in which 100,000 copies are continuously produced was performed using each developer and the copier IMAGIO MF6550 which had been modified such that the fixing device is replaced with a fixer having such a structure as illustrated in FIG. 2. The image density of the 100,000th image was measured with a MACBETH densitometer. The greater the image density, the greater blackness the toner has.

(2) Toner scattering

[0182] A running test in which 100,000 copies are continuously produced was performed using each developer and

the copier IMAGIO MF6550 which had been modified such that the fixing device is replaced with a fixer having such a structure as illustrated in FIG. 2 while a white paper is attached to the inside wall of the front door of the copier. The density of the white paper was 0.07 before the running test. The greater the density, the worse toner scattering property the toner has.

(4) Background fouling

[0183] After the 100,000-copy running test, the 100,000th image was visually observed to determine whether the image has background fouling. Background fouling is graded into the following four ranks:

- ⊙ : the image has no background fouling. (excellent)
- : the image has slight background fouling. (good)
- △ : the image has background fouling but is still acceptable.
- X : the image has serious background fouling. (bad)

[0184] The evaluation results are shown in Tables 2-1 to 2-3 below.

Example 2

[0185] The procedure for preparation of the toner particles in Example 1 was repeated except that the formula was changed as follows and the kneading was performed for 10 minutes at 150 °C.

Styrene-methacrylate copolymer (THF-insoluble component content of 0 %; Tg of 75 °C)	76 parts
Black iron oxide compound No. 2	18 parts
Carnauba wax	4 parts
Charge controlling agent (zinc salicylate E-84 from Orient Chemical Industries Co., Ltd.)	2 parts

[0186] Thus, toner particles having a weight average particle diameter of 2.5 μm were prepared.

[0187] Then 1.5 parts of a silica powder HDK-1303VP from Clariant Japan K.K. were mixed with 100 parts of the toner particles using a Henschel mixer.

[0188] Thus, a toner of Example 2 was prepared.

[0189] The toner was evaluated in the same way as that in Example 1 and the evaluation results of the toner are also shown in Tables 2-1 to 2-3.

Example 3

[0190] The procedure for preparation of the toner particles in Example 1 was repeated except that the formula was changed as follows and the kneading was performed for 10 minutes at 150 °C.

Styrene-methacrylate copolymer (THF-insoluble component content of 0 %; Tg of 75 °C)	76 parts
Black iron oxide compound No. 2	18 parts
Carnauba wax	4 parts
Charge controlling agent (zirconium salicylate TN-105 from Hodogaya Chemical Co., Ltd.)	2 parts

[0191] Thus, toner particles having a weight average particle diameter of 2.5 μm were prepared.

[0192] Then 1.5 parts of a silica powder R-972 from Clariant Japan K.K. were mixed with 100 parts of the toner particles using a Henschel mixer.

[0193] Thus, a toner of Example 3 was prepared.

[0194] The toner was evaluated in the same way as that in Example 1 and the evaluation results of the toner are also shown in Tables 2-1 to 2-3.

Example 4

[0195] The procedure for preparation of the toner particles in Example 1 was repeated except that the formula was changed as follows and the kneading was performed for 10 minutes at 150 °C.

Polyester resin (THF-insoluble component content of 0 %; Tg of 55 °C)	71 parts
Black iron oxide compound No. 3	21 parts
Carnauba wax	6 parts
Charge controlling agent (zirconium salicylate TN-105 from Hodogaya Chemical Co., Ltd.)	2 parts

[0196] Thus, toner particles having a weight average particle diameter of 7.2 μm were prepared.

[0197] Then 1.5 parts of a silica powder R-972 from Clariant Japan K.K. were mixed with 100 parts of the toner particles using a Henschel mixer.

[0198] Thus, a toner of Example 4 was prepared.

[0199] The toner was evaluated in the same way as that in Example 1 and the evaluation results of the toner are also shown in Tables 2-1 to 2-3.

Example 5

[0200] The procedure for preparation of the toner particles in Example 1 was repeated except that the formula was changed as follows and the kneading was performed for 10 minutes at 130 °C.

Polyester resin (THF-insoluble component content of 20 %; Tg of 70 °C)	35 parts
Polyester resin (THF-insoluble component content of 0 %; Tg of 65 °C)	30 parts
Black iron oxide compound No. 4	30 parts
Carnauba wax	3 parts
Charge controlling agent (zirconium salicylate TN-105 from Hodogaya Chemical Co., Ltd.)	2 parts

[0201] Thus, toner particles having a weight average particle diameter of 6.8 μm were prepared.

[0202] Then 0.5 parts of a silica powder HDK-1303VP from Clariant Japan K. K. and 0.1 parts of a titanium oxide SMT-600BI from Tayca Corp. were mixed with 100 parts of the toner particles using a Henschel mixer.

[0203] Thus, a toner of Example 5 was prepared.

[0204] The toner was evaluated in the same way as that in Example 1 and the evaluation results of the toner are also shown in Tables 2-1 to 2-3.

Example 6

[0205] The following components were mixed.

Polyester resin (THF-insoluble component content of 0 %; Tg of 60 °C)	1 part
Black iron oxide compound No. 5	1 part
Pure water	0.5 parts

[0206] The mixture was kneaded at 70 °C using a two-roll mill. Then the temperature of the two-roll mill was increased to 120 °C to remove water from the kneaded mixture. Thus, a masterbatch B was prepared.

[0207] The procedure for preparation of the toner particles in Example 1 was repeated except that the formula was changed as follows and the kneading was performed for 10 minutes at 150 °C.

Masterbatch B prepared above	50 parts
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(continued)

Styrene-n-butyl acrylate (THF-insoluble component content of 25 %; Tg of 50 °C)	10 parts
Polyester resin (THF-insoluble component content of 10 %; Tg of 55 °C)	30 parts
Rice wax	7 parts
Charge controlling agent (zirconium salicylate TN-105 from Hodogaya Chemical Co., Ltd.)	3 parts

[0208] Thus, toner particles having a weight average particle diameter of 5.5 µm were prepared.

[0209] Then 0.7 parts of a silica powder R-972 from Clariant Japan K. K. and 0.3 parts of a titanium oxide SMT-600BI from Tayca Corp. were mixed with 100 parts of the toner particles using a Henschel mixer.

[0210] Thus, a toner of Example 6 was prepared.

[0211] The toner was evaluated in the same way as that in Example 1 and the evaluation results of the toner are also shown in Tables 2-1 to 2-3.

Example 7

[0212] The procedure for preparation of the masterbatch B in Example 6 was repeated except that the formula was changed as follows.

Formula of masterbatch C	
Polyester resin (THF-insoluble component content of 0 %; Tg of 60 °C)	1 part
Black iron oxide compound No. 6	1 part
Pure water	0.5 parts

[0213] The procedure for preparation of the toner particles in Example 1 was repeated except that the formula was changed as follows and the kneading was performed for 15 minutes at 130 °C.

Formula of toner particles	
Masterbatch C prepared above	52 parts
Styrene-methacrylic acid copolymer (THF-insoluble component content of 0 %; Tg of 62 °C)	5 parts
Polyester resin (THF-insoluble component content of 25 %; Tg of 65 °C)	36 parts
Ester wax	6 parts
Charge controlling agent (zirconium salicylate TN-105 from Hodogaya Chemical Co., Ltd.)	1 part

[0214] Thus, toner particles having a weight average particle diameter of 3.5 µm were prepared.

[0215] Then 0.7 parts of a silica powder R-972 from Clariant Japan K. K. and 0.3 parts of a titanium oxide SMT-600BI from Tayca Corp. were mixed with 100 parts of the toner particles using a Henschel mixer.

[0216] Thus, a toner of Example 7 was prepared.

[0217] The toner was evaluated in the same way as that in Example 1 and the evaluation results of the toner are also shown in Tables 2-1 to 2-3.

Example 8

[0218] The procedure for preparation of the masterbatch B in Example 6 was repeated except that the formula was changed as follows.

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Formula of masterbatch D	
Polyester resin (THF-insoluble component content of 0 %; Tg of 60 °C)	1 part
Black iron oxide compound No. 7	1 part
Pure water	0.5 parts

[0219] The procedure for preparation of the toner particles in Example 1 was repeated except that the formula was changed as follows and the kneading was performed for 30 minutes at 130 °C.

Formula of toner particles	
Masterbatch D prepared above	58 parts
Polyester resin (THF-insoluble component content of 40 %; Tg of 60 °C)	32 parts
Carnauba wax	6 parts
Charge controlling agent (zirconium salicylate TN-105 from Hodogaya Chemical Co., Ltd.)	4 parts

[0220] Thus, toner particles having a weight average particle diameter of 4.2 μm were prepared.

[0221] Then 1.8 parts of a silica powder R-972 from Clariant Japan K.K. and 0.5 parts of a titanium oxide SW-100 from Titan Kogyo K.K. were mixed with 100 parts of the toner particles using a Henschel mixer.

[0222] Thus, a toner of Example 8 was prepared.

[0223] The toner was evaluated in the same way as that in Example 1 and the evaluation results of the toner are also shown in Tables 2-1 to 2-3.

Example 9

[0224] The procedure for preparation of the masterbatch B in Example 6 was repeated except that the formula was changed as follows.

Formula of masterbatch E	
Polyester resin A (THF-insoluble component content of 0 %; Tg of 65 °C)	1 part
Black iron oxide compound No. 8	1 part
Pure water	0.5 parts

[0225] The procedure for preparation of the toner particles in Example 1 was repeated except that the formula was changed as follows.

Formula of toner particles	
Masterbatch E prepared above	60 parts
Styrene-n-butyl methacrylate copolymer (THF-insoluble component content of 10 %; Tg of 58 °C)	10 parts
Polyester resin A	28 parts
Carnauba wax	5 parts
Charge controlling agent (zirconium salicylate TN-105 from Hodogaya Chemical Co., Ltd.)	2 parts

[0226] Thus, toner particles having a weight average particle diameter of 4.5 μm were prepared.

[0227] Then 3.0 parts of a silica powder HDK-1301VP from Clariant Japan K. K. were mixed with 100 parts of the toner particles using a Henschel mixer.

[0228] Thus, a toner of Example 9 was prepared.

[0229] The toner was evaluated in the same way as that in Example 1 and the evaluation results of the toner are

also shown in Tables 2-1 to 2-3.

Example 10

[0230] The procedure for preparation of the masterbatch B in Example 6 was repeated except that the formula was changed as follows.

Formula of masterbatch F	
Polyester resin B (THF-insoluble component content of 0 %; Tg of 55 °C)	1 part
Black iron oxide compound No. 9	1 part
Pure water	0.5 parts

[0231] The procedure for preparation of the toner particles in Example 1 was repeated except that the formula was changed as follows.

Formula of toner particles	
Masterbatch F prepared above	50 parts
Polyester resin (THF-insoluble component content of 30 %; Tg of 58 °C)	30 parts
Polyester resin B	10 parts
Carnauba wax	7 parts
Charge controlling agent (zirconium salicylate TN-105 from Hodogaya Chemical Co., Ltd.)	3 parts

[0232] Thus, toner particles having a weight average particle diameter of 6.0 μm were prepared.

[0233] Then 2.0 parts of a silica powder HDK-1301VP from Clariant Japan K. K. were mixed with 100 parts of the toner particles using a Henschel mixer.

[0234] Thus, a toner of Example 10 was prepared.

[0235] The toner was evaluated in the same way as that in Example 1 and the evaluation results of the toner are also shown in Tables 2-1 to 2-3.

Comparative Example 1

[0236] The procedure for preparation of the masterbatch B in Example 6 was repeated except that the formula was changed as follows.

Formula of masterbatch G	
Polyester resin B	1 part
Black iron oxide compound No. 10	1 part
Pure water	0.5 parts

[0237] The procedure for preparation of the toner particles in Example 1 was repeated except that the formula was changed as follows.

Formula of toner particles	
Masterbatch G prepared above	50 parts
Polyester resin (THF-insoluble component content of 30 %; Tg of 58 °C)	30 parts
Polyester resin B	10 parts
Carnauba wax	7 parts
Charge controlling agent (zirconium salicylate TN-105 from Hodogaya Chemical Co., Ltd.)	3 parts

[0238] Thus, toner particles having a weight average particle diameter of 6.0 μm were prepared.

[0239] Then 2.0 parts of a silica powder HDK-1301VP from Clariant Japan K. K. were mixed with 100 parts of the toner particles using a Henschel mixer.

[0240] Thus, a toner of Comparative Example 1 was prepared.

[0241] The toner was evaluated in the same way as that in Example 1 and the evaluation results of the toner are also shown in Tables 2-1 to 2-3.

Comparative Example 2

[0242] The procedure for preparation of the toner particles in Example 1 was repeated except that the formula was changed as follows and the kneading was performed for 10 minutes at 150 °C.

Formula of toner particles	
Masterbatch G prepared above	50 parts
Styrene-n-butyl methacrylate copolymer (THF-insoluble component content of 20 %; Tg of 69 °C)	10 parts
Polyester resin B	30 parts
Carnauba wax	7 parts
Charge controlling agent (zirconium salicylate TN-105 from Hodogaya Chemical Co., Ltd.)	3 parts

[0243] Thus, toner particles having a weight average particle diameter of 6.5 μm were prepared.

[0244] Then 0.5 parts of a silica powder R-972 from Clariant Japan K.K. and 0.2 parts of a titanium oxide were mixed with 100 parts of the toner particles using a Henschel mixer.

[0245] Thus, a toner of Comparative Example 2 was prepared.

[0246] The toner was evaluated in the same way as that in Example 1 and the evaluation results of the toner are also shown in Tables 2-1 to 2-3.

Comparative Example 3

[0247] The procedure for preparation of the toner particles in Example 1 was repeated except that the formula was changed as follows and the kneading was performed for 10 minutes at 150 °C.

Formula of toner particles	
Polyester resin (THF-insoluble component content of 20 %; Tg of 59 °C)	50 parts
Polyester resin (THF-insoluble component content of 0 %; Tg of 59 °C)	20 parts
Black iron oxide compound 12	20 parts
Carnauba wax	7 parts
Charge controlling agent (zirconium salicylate TN-105 from Hodogaya Chemical Co., Ltd.)	3 parts

[0248] Thus, toner particles having a weight average particle diameter of 6.0 μm were prepared.

[0249] Then 0.5 parts of a silica powder R-972 from Clariant Japan K.K. and 1.2 parts of a titanium oxide were mixed with 100 parts of the toner particles using a Henschel mixer.

[0250] Thus, a toner of Comparative Example 3 was prepared.

[0251] The toner was evaluated in the same way as that in Example 1 and the evaluation results of the toner are also shown in Tables 2-1 to 2-3.

Table 2-1

	H* (kA/m)	σs^{**} (Am ² /Kg)	Content of colorant (wt%)	Specific gravity of toner	Vlume resistivity in log scale ($\Omega \cdot \text{cm}$)	L* a* b *
Ex. 1	10	7	35	1.60	10.5	28 -1.0 0.2
Ex. 2	3	3	18	1.28	11.7	25 0.6 - 0.9
Ex. 3	2	3	18	1.26	11.6	22 -0.8 - 0.5
Ex. 4	2	2.2	21	1.35	10.6	20 -0.8 - 0.5
Ex. 5	5	1.5	30	1.40	11.4	18 -0.5 0.4
Ex. 6	15	15	25	1.38	11.0	15 -1.0 0.8
Ex. 7	8	0.2	26	1.37	11.2	12 0.6 - 0.2
Ex. 8	10	4.2	29	1.42	10.9	13 0.2 - 0.8
Ex. 9	4	5	29	1.35	11.2	12 -0.6 0.3
Ex. 10	12	1.5	30	1.50	11.3	10 -0.5 0.3
Comp. Ex. 1	25	10	25	1.42	10.9	34 -3.2 - 2.1
Comp. Ex. 2	0.5	3	25	1.50	10.9	37 3.1 3.4
Comp. Ex. 3	0.5	2	20	1.38	11.3	32 2.8 - 3.6

H*: coercive force of the toner

 σs^{**} : saturation magnetization of the toner

Table 2-2

	MI (g/10min)	Tg (°C)	Mp	Image density	Toner scattering
Ex. 1	8	70	6000	1.32	0.10
Ex. 2	22	75	3000	1.35	0.09
Ex. 3	15	75	3000	1.38	0.09
Ex. 4	5	52	8000	1.40	0.07
Ex. 5	25	68	10000	1.42	0.09
Ex. 6	20	53	2500	1.45	0.08
Ex. 7	18	60	3500	1.45	0.08
Ex. 8	16	60	3800	1.44	0.07
Ex. 9	12	58	4900	1.45	0.07
Ex. 10	16	59	5200	1.46	0.07
Comp. Ex. 1	15	59	3400	1.18	0.09
Comp. Ex. 2	18	56	5200	1.08	0.34
Comp. Ex. 3	12	60	4400	0.98	0.42

Table 2-3

	MFT*(°C)	HOT**(°C)	Pulverization speed (kg/h)	Background fouling	Color tone of image
Ex. 1	160	230	7	Δ	Black
Ex. 2	150	220	10	○	Black and clear
Ex. 3	150	250	10	⊙	Black and clear
Ex. 4	150	250	6	⊙	Black and clear
Ex. 5	140	250	8	⊙	Black and clear
Ex. 6	130	220	13	⊙	Soft black color
Ex. 7	130	250	12	⊙	Soft black color
Ex. 8	130	250	10	⊙	Soft black color
Ex. 9	130	250	12	⊙	Soft black color
Ex. 10	130	250	11	⊙	Soft black color
Comp. Ex. 1	190	230	8	⊙	Light black and unclear
Comp. Ex. 2	170	240	10	X	Light black and unclear
Comp. Ex. 3	180	240	10	X	Light black and unclear

MFT*: minimum fixable temperature of the toner

HOT**: hot offset temperature of the toner

Effects of the present invention

[0252] The toner of the present invention has good fixability, high blackness, good pulverizability and high safety, and can produce images with high image density without causing the toner scattering problem.

[0253] When the toner has a weight average particle diameter D₄ of from 3 to 10 μm, the low temperature fixability and blackness of the toner can be further improved.

[0254] When the black iron oxide compound has an average primary particle diameter of from 0.005 to 1.5 μm, the black iron oxide compound can be well dispersed in the toner, and thereby the pulverizability and low temperature fixability can be further improved.

[0255] When the toner has a melt index (MI) of from 10 to 20 g/min, the low temperature fixability of the toner can be further improved. Therefore, the toner can be used for high speed image forming apparatus and energy-saved image forming apparatus.

[0256] When the toner has a glass transition temperature (T_g) of from 55 to 65 °C, the toner has a good combination of low temperature fixability and preservability.

[0257] When the toner includes a carnauba wax, a rice wax and/or an ester wax, wherein the content of the wax is from 0.5 to 7 % by weight based on the total weight of the toner, the toner does not cause a hot offset problem even when used for oil-less fixing devices. In addition, the toner has good low temperature fixability and high blackness.

[0258] When tetrahydrofuran-soluble components of the toner have a molecular weight distribution such that a peak molecular weight M_p is present in a molecular weight range of from 3300 to 5500, the toner has good low temperature fixability and good pulverizability (i.e., productivity).

[0259] The two component developer of the present invention can produce high quality images even when used for low pressure fixing devices having a thin roller.

[0260] In addition, high quality images can be produced by the image forming method without causing the toner scattering problem even when a low pressure fixing device having a thin roller is used.

[0261] This document claims priority and contains subject matter related to Japanese Patent Applications Nos. 2003-203177 and 2003-305302, filed on July 29, 2003, and August 28, 2003, respectively.

Claims

1. A toner comprising:

a binder resin; and

a colorant comprising an iron oxide compound including Ti in such an amount that the weight of Ti atom is from 10 to 45 % by weight based on the weight of Fe atom therein when measured with a wavelength dispersive fluorescent X-ray analyzer,

wherein the content of the black iron oxide compound in the toner is from 15 to 40 % by weight, and the coercive force of the toner is from 2 to 15 kA/m in a magnetic field of 398 Am²/Kg when measured with a multi-sample rotation type magnetization measurement system from Toei Industry Co., Ltd.

2. The toner according to Claim 1, wherein the toner has a saturation magnetization σ_s of from 0.1 to 5.0 Am²/Kg.

3. The toner according to Claim 1 or 2, wherein the toner has a true specific gravity of from 1.35 to 1.55.

4. The toner according to any one of Claims 1 to 3, wherein the volume resistivity of the toner is from 10.9 to 11.4 Ω · cm in logarithmic scale.

5. The toner according to any one of Claims 1 to 4, wherein the black iron oxide compound is included in the toner in an amount of from 21 to 30 % by weight based on the total weight of the toner.

6. The toner according to any one of Claims 1 to 5, further comprising:

a zirconium compound selected from the group consisting of Zr-containing aromatic oxycarboxylic acids and Zr-containing aromatic oxycarboxylic acid salts.

7. The toner according to any one of Claims 1 to 6, wherein when a solid image of the toner having a weight of 0.60 to 0.85 mg/cm² is fixed on an art paper classified into TYPE 1 specified in ISO 12647-2 and the color of the fixed solid image is measured by a method specified in ISO 12647-1 using a colorimeter X-Rite 938 to determine L *, a * and b *, the solid image satisfies the following relationships:

$$10 \leq L^* \leq 28, -1.0 \leq a^* \leq 1.0, \text{ and } -1.0 \leq b^* \leq 1.0.$$

- 5 8. The toner according to any one of Claims 1 to 7, wherein the toner has a weight average particle diameter D₄ of from 3 to 10 μm.
9. The toner according to any one of Claims 1 to 8, wherein the black iron oxide compound has an average primary particle diameter of from 0.005 to 1.5 μm.
- 10 10. The toner according to any one of Claims 1 to 9, wherein the toner has a melt index (MI) of from 10 to 20 g/min when the melt index is measured by a method specified in JIS K 6760 under conditions of 150 °C in temperature and 2160 g in load.
- 15 11. The toner according to any one of Claims 1 to 10, wherein the toner has a glass transition temperature (T_g) of from 55 to 65 °C.
12. The toner according to any one of Claims 1 to 11, further comprising:
a wax selected from the group consisting of carnauba waxes, rice waxes and ester waxes, in an amount of
20 from 0.5 to 7 % by weight based on the total weight of the toner.
13. The toner according to any one of Claims 1 to 12, wherein tetrahydrofuran-soluble components of the toner have a molecular weight distribution such that a peak molecular weight M_p is present in a molecular weight range of from 3300 to 5500 when the molecular weight distribution is determined by gel permeation chromatography.
- 25 14. A toner container containing a toner according to any one of Claims 1 to 13.
15. A two-component developer comprising:
a carrier; and
a toner according to any one of claims 1 to 13.
- 30 16. An image forming method comprising:
charging an image bearing member (1; 31);
forming an electrostatic latent image on the charged image bearing member;
developing the electrostatic latent image with a developer including a toner according to any one of Claims 1 to 13 to form a toner image on the image bearing member;
transferring the toner image on a receiving material (S);
40 fixing the toner image on the receiving material; and
cleaning a surface of the image bearing member.
17. The image forming method according to Claim 16, wherein the fixing is performed by passing the receiving material (S) having the toner image thereon into a pair of rollers (21, 22), wherein the roller (21) contacting the toner image is a cylinder (23) having a thickness not greater than 1.0 mm and a pressure applied to the pair of rollers is not greater than 1.5 x 10⁵ Pa.
- 45 18. The image forming method according to Claim 16 or 17, wherein the toner collected by cleaning the surface of the image bearing member (1; 31) is re-used for developing.
- 50 19. The image forming method according to any one of Claims 16 to 18, wherein the charging is performed using a contact charger (32).
20. The image forming method according to any one of Claims 16 to 19, wherein the image transferring is performed by contacting a transfer member (5) to the image bearing member (1; 31) with the receiving material (S) therebetween while applying a voltage to the transfer member.
- 55 21. A process cartridge (30) comprising:

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a developing device (33) configured to develop an electrostatic latent image on an image bearing member (31) with a developer comprising a toner according to any one of Claims 1 to 13; and
a housing (35).

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FIG. 1

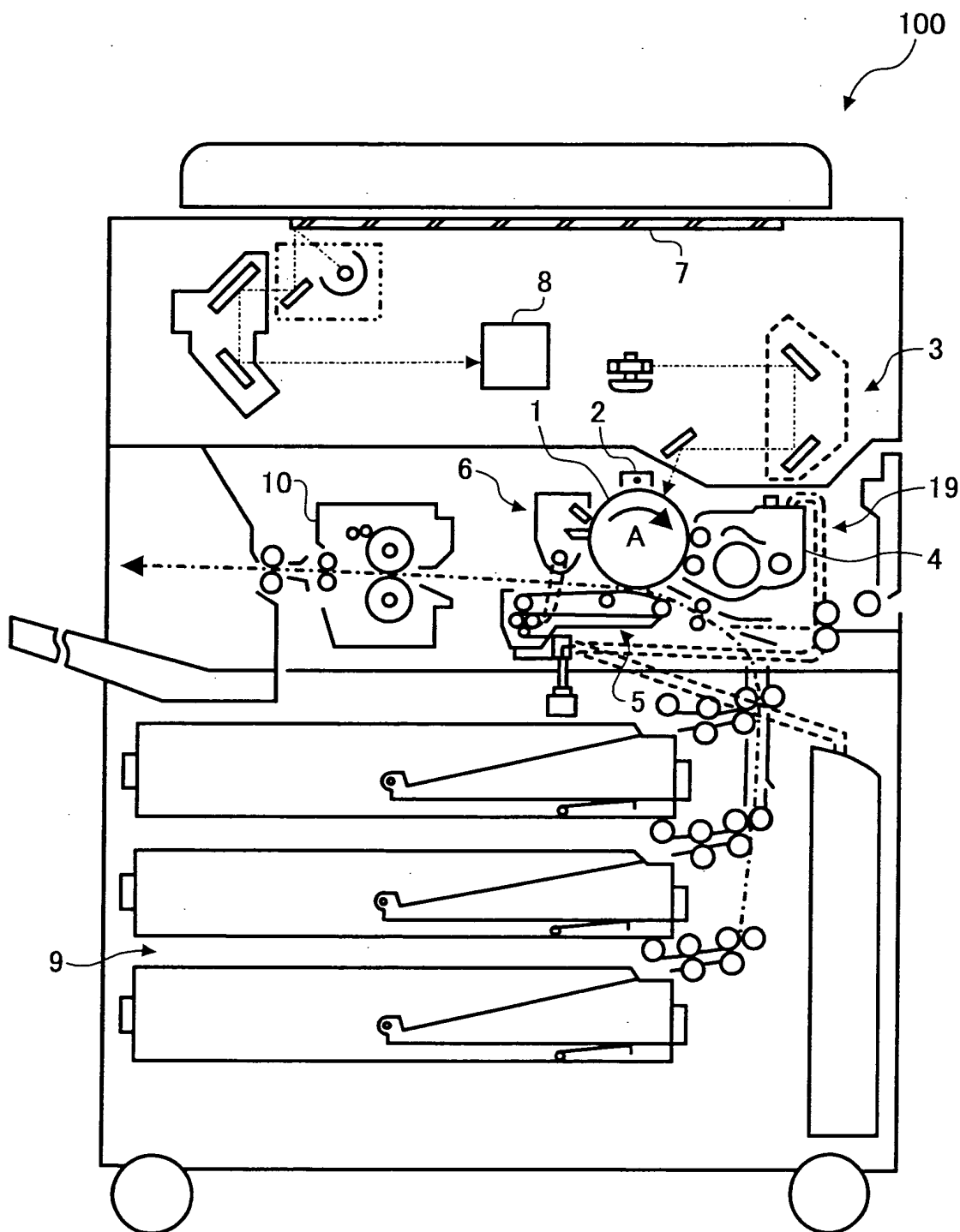


FIG. 2

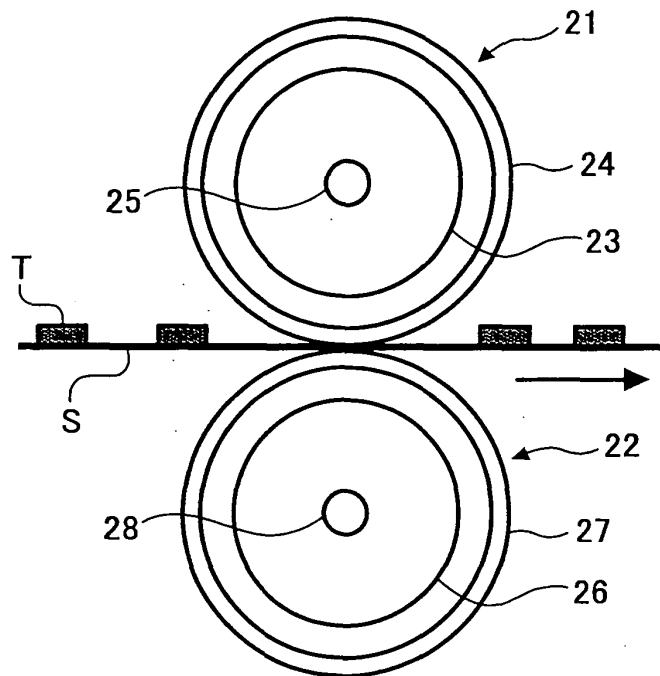


FIG. 3

