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(54) Electrophotographic toner

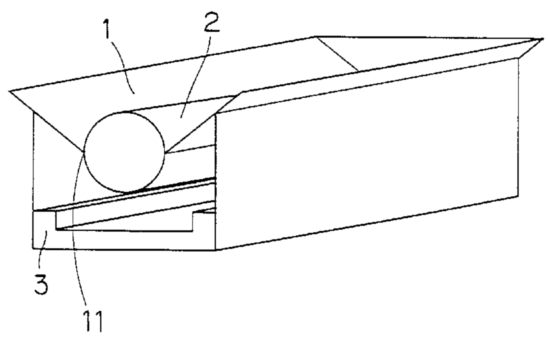
(57) There can be provided an electrophotographic toner having a small particle size, which is superior in fluidity, charging properties and charging stability, obtained by treating a surface of a toner particle with a hydrophobic fine silica particle treated with hexamethyldisilazane and at least one of the following:

(a) fine titanium oxide particles treated with a polyhydric alcohol,

(b) fine titanium oxide particles having a resistivity of 10^6 to 10^8 Ω.cm, and

(c) fine titanium oxide particles wherein the absolute charged amount obtained when it is charged by mixing with a magnetic carrier is 5 to 80 μC/g and the charging polarity is the same as that of the toner.

FIG. 1



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Description

BACKGROUND OF THE INVENTION

This invention relates to an electrophotographic toner. More particularly, it relates to an electrophotographic toner having a small particle size, which is used to attain a high image quality of the image formed.

In addition to a magnetic toner as a one-component developer, a two-component developer comprising a toner and a magnetic carrier is used for the development in image forming apparatuses such as electrostatic copying machine, laser beam printer and the like.

The toner to be used for the two-component developer is normally produced by blending a colorant (e.g. carbon black, etc.), an electric charge controlling material, etc. in a fixing resin, and then kneading, pulverizing, classifying and granulating the mixture to give a particle having a predetermined particle size. Further, regarding such an electrophotographic toner, a surface treatment is conducted by adhering an additive of a fine particle having a particle size smaller than that of a toner particle on the surface of the toner particle so as to improve the fluidity, charging properties and charging stability.

Recently, a toner having a small particle size of not more than 9 μm has been put into practical use for the purpose of attaining a higher image quality of the image formed. However, since such a toner having a small particle size is inferior in fluidity in comparison with a conventional one, there is a problem that the toner is liable to cause blocking to form a toner agglomerate. Further, since the toner having a small particle size is unstable in charging properties in comparison with a conventional one, there is a also problem that toner scattering due to charging failure, or image failure (e.g. fog caused by adhering the toner on the blank space area of the image formed, etc.) is liable to arise.

Therefore, in order to solve these problems, the use of a fine silica particle in combination with a fine titanium oxide particle as the additive for treating the surface of the toner has been studied.

In the additive for the surface treatment, the fine silica particle mainly serves to improve the fluidity of the toner particle and to increase the charged amount of the whole toner. On the other hand, the fine titanium oxide particle serves to make the charged amount of the whole toner particle uniform by assisting the movement of electric charges between toner particles to prevent a highly charged toner having the charged amount exceeding a predetermined charged amount, a weakly charged toner having the charged amount less than the predetermined charged amount and a inversely charged toner to be charged to an inverse polarity from generating, thereby stabilizing the charging properties of the toner.

However, according to the study of the inventors regarding the additive for treating the surface of the toner having a small particle size, it has been found that the above effect cannot be sufficiently obtained merely by using the fine silica particle in combination with the fine titanium oxide particle.

As the fine silica particle in the additive for the surface treatment, there can be normally used a hydrophobic fine silica particle which can impart the moisture resistance and shelf stability to the toner. Examples of the hydrophobic fine silica particle include a fine silica particle having a high hydrophobicity obtained by burning and hydrolyzing a volatile silicon compound (e.g. silicon tetrachloride, etc.) in a vapor phase and treating a silanol group on the surface of the particle of the resulting fumed silica with organosilane (e.g. dichlorodimethylsilane, etc.) or organosiloxane (e.g. dimethylpolysiloxane, etc.); an arc method fine silica particle obtained by burning silicon monoxide to be volatilized from an arc furnace; and the like. However, since any conventional hydrophobic fine silica particle is liable to agglomerate and does not easily adhere on the surface of the toner particle, uniformly, it is necessary to add a large amount of the fine silica particle to impart the sufficient fluidity to the toner particle.

When a large amount of the fine particle is added like this, a problem arises that the charge amount of the whole toner becomes too large. Further, the excessive hydrophobic fine silica particle adheres on the surface of the fine titanium oxide particle to prevent the fine titanium oxide particle from adhering on the surface of the toner particle so that the effect of assisting the movement of electric charge between toner particles cannot be sufficiently obtained. As a result, the distribution of the charged amount of the toner particle is widened to generate the highly charged toner, weakly charged toner and inversely charged toner, thereby causing image failure such as toner scattering, fog, etc.

On the other hand, when a large amount of the fine titanium oxide particle is added so as to prevent such a phenomenon, a problem arises that the image density of the image formed is decreased.

SUMMARY OF THE INVENTION

It is a main object of this invention to provide a novel electrophotographic toner having a small particle size, which is superior in fluidity, charging properties and charging stability.

Firstly, the inventors have studied intensively about a hydrophobic fine silica particle for treating the surface of the toner, in order to accomplish the above object.

As a result, it has been found that there can be obtained a hydrophobic fine silica particle, which does not easily agglomerate and is liable to adhere on the surface of the toner particle uniformly, and which is superior in effect for improving the fluidity of the toner particle, by treating a silanol group on the surface of the silica particle with hexamethyldisilazane to silylate it. Further, it has also been found that the amount of the hydrophobic fine silica particle required to obtain a predetermined charged amount is small and the amount of the hydrophobic fine silica particle to be adhered on the surface of the fine titanium oxide particle is small when the toner particle is subjected to the surface treatment using the hydrophobic fine silica particle and, therefore, the effect for assisting the movement of electric charges between toner particles is not disturbed.

Then, the inventors have studied intensively about the fine titanium oxide particle to be used in combination with the hydrophobic fine silica particle treated with hexamethyldisilazane. As a result, an optimum combination capable of providing a toner, which is superior in fluidity, charging properties and charging stability, has been found, thus this invention has been accomplished.

That is, the electrophotographic toner of this invention comprises a toner particle and an additive for treating a surface of the toner, the additive comprising a combination of a hydrophobic fine silica particle treated with hexamethyldisilazane and at least one of the following fine titanium oxide particles (a) to (c):

(a) fine titanium oxide particle treated with a polyhydric alcohol,

(b) fine titanium oxide particle having a resistivity of 10^6 to 10^8 $\Omega\cdot$cm, and

(c) fine titanium oxide particle wherein an absolute charged amount obtained when it is charged by mixing with a magnetic carrier to be used for charging the toner particle is 5 to 80 μC/g and a charging polarity is the same as that of the toner.

In the electrophotographic toner, the fine titanium oxide particle treated with the polyhydric alcohol to be used in combination with the hydrophobic fine silica particle treated with hexamethyldisilazane does not easily agglomerate and can adhere uniformly on the surface of the toner particle together with the hydrophobic silica, so that it is superior in effect for assisting the movement of electric charges between toner particles.

In addition, since the fine titanium oxide particle having a resistivity of 10^6 to 10^8 $\Omega\cdot$cm has a suitable electric charge moving capability to the toner particle, the movement of electric charges between toner particles is smoothly conducted and, therefore, it is superior in effect for making the charged amount of the whole toner uniform.

Further, the fine titanium oxide particle, wherein an absolute charged amount obtained when it is charged by mixing with a magnetic carrier to be used for charging the toner particle is 5 to 80 μC/g and a charging polarity is the same as that of the toner, has a suitable electric charge moving capability to the toner particle, similar to the fine titanium oxide particle having a resistivity of 10^6 to 10^8 $\Omega\cdot$cm. Therefore, the movement of electric charges between toner particles is smoothly conducted so that it is superior in effect for making the charged amount of the whole toner uniform.

Accordingly, the electrophotographic toner of this invention comprising at least one of the above three sorts of fine titanium oxide particles in combination with the above hydrophobic fine silica particle is superior in fluidity, charging properties and charging stability.

Other objects and advantages of this invention will become apparent to those skilled in the art from the following description of embodiments of the invention.

BRIEF EXPLANATION OF DRAWINGS

Fig. **1** is a perspective view illustrating an apparatus for evaluating the fluidity of a toner.

DETAILED DESCRIPTION OF THE INVENTION

The hydrophobic fine silica particles to be used in this invention may be those in which a silanol group on the surface of the silica fine particle is treated with hexamethyldisilazane. Examples of the hydrophobic fine silica particle include Aerogyl R812 and RX200 manufactured by Nihon Aerogyl Co., Ltd.

As example of the silica fine particle which is the raw material for the above hydrophobic fine silica particle, there can be suitably used a fumed silica obtained by burning and hydrolyzing a volatile silicon compound (e.g. silicon tetrachloride, etc.) in a vapor phase as described above.

In order to treat a silanol group on the surface of the silica fine particle with hexamethyldisilazane to silylate it, the silica fine particle may be reacted with hexamethyldisilazane in a reaction column of a fluid bed.

The hydrophobic fine silica particle is superior in effect for improving the fluidity of the toner particle, as described above, because it does not easily agglomerate in comparison with a conventional hydrophobic silica. Further, it exhibits a high hydrophobicity because the silanol group is scarcely present on the surface thereof and, therefore, the moisture-resistance and shelf stability of the toner can be extremely improved.

The particle size of the hydrophobic fine silica particle is not specifically limited in this invention, but the average particle size of a primary particle is preferably about 5 to 50 nm in view of the production process when using the above fumed silica. Further, it is preferred that the particle size distribution is sharp within a range of the above particle size, in order to obtain stable charging characteristics and fluidity. When the particle size of the hydrophobic fine silica particle is smaller than the above range, the hydrophobic fine silica particles are likely to agglomerate. On the other hand, when the particle size exceeds the above range, the effect for improving the fluidity of the toner particle is likely to become insufficient. Further, the average particle size of the hydrophobic fine silica particle (primary particle) is preferably 7 to 30 nm, more preferably 10 to 20 nm, in order to obtain a toner having stable charging characteristics and fluidity.

The amount of the hydrophobic fine silica particle to be added is preferably about 0.01 to 5 parts by weight, more preferably 0.05 to 2 parts by weight, most preferably 0.1 to 1 parts by weight, based on 100 parts by weight of the toner particle.

When the amount of the hydrophobic fine silica particle is smaller than the above range, the effect for improving the fluidity of the toner particle tends to become insufficient, thereby causing blocking to form a toner agglomerate. Further, since no effect for increasing the charged amount of the whole toner is obtained, the charged amount of the toner tends to become insufficient, thereby causing image failure such as decrease in image density of the image formed.

On the other hand, when the amount of the hydrophobic fine silica particle exceeds the above range, the charged amount of the whole toner tends to become too large. In addition, the excessive hydrophobic fine silica particle is liable to adhere on the surface of the fine titanium oxide particle to prevent the fine titanium oxide particle from adhering on the surface of the toner particle, thereby obtaining the insufficient effect for assisting the movement of electric charges between toner particles. As a result, such a problem arises that the distribution of the charged amount is widen to generate the highly charged toner, weakly charged toner and inversely charged toner, thereby causing image failure such as toner scattering, fog, etc.

As the fine titanium oxide particle to be used in this invention, there are fine titanium oxide particles (a) to (c) as described above.

The fine titanium oxide particle (a) can be obtained by sintering, pulverizing and classifying a titanium oxide particle to give a fine titanium particle, followed by treating the surface of the fine particle with a polyhydric alcohol.

Examples of the polyhydric alcohol include trimethylolpropane represented by the formula:

$$CH_3\text{-}CH_2\text{-}C(CH_2OH)_3 \qquad (1)$$

and pentaerythritol represented by the formula:

$$C(CH_2OH)_4 \qquad (2)$$

In order to treat the surface of the fine titanium oxide particle with the polyhydric alcohol, the polyhydric alcohol may be added at the final stage of the pulverization of the titanium oxide particle, followed by mixing. This mixing enables a hydroxyl group of the polyhydric alcohol to bond to a hydrophilic group of a fine titanium oxide particle newly produced by the pulverization, thereby deteriorating agglomeration properties of the fine titanium oxide particle.

The particle size of the fine titanium oxide particle (a) is not specifically limited in this invention, but the average particle size of the primary particle thereof is preferably about 10 to 200 nm.

When the particle size of the fine titanium oxide particle is smaller than the above range, the fine titanium particles tend to agglomerate. On the other hand, when the particle size exceeds the above range, the surface of a photoconductor is liable to be scraped by the fine titanium oxide particle, that is, so-called "drum scraping" tends to arise when using the toner obtained by using the titanium oxide. Further, the average particle size of the fine titanium oxide particle (primary particle) is preferably 20 to 100 nm, more preferably 30 to 80 nm, in order to obtain a toner having stable charging characteristics and fluidity.

A convenient amount of the fine titanium oxide particle to be added is about 0.01 to 10 parts by weight, preferably 0.05 to 3 parts by weight, more preferably 0.1 to 2 parts by weight, based on 100 parts by weight of the toner particle.

When the amount of the fine titanium oxide particle is smaller than the above range, the charged amount of the whole toner tends to become too large and, at the same time, the effect for assisting the movement of electric charges between toner particles becomes insufficient. Therefore, the distribution of the charged amount is widen to generate the highly charged toner, weakly charged toner and inversely charged toner, thereby causing image failure such as toner scattering, fog, etc.

On the other hand, when the amount of the fine titanium oxide particle exceeds the above range, the charged amount of the whole toner tends to decrease, thereby causing image failure such as decrease in image density of the image formed, as described above.

The fine titanium oxide particle of (b) is limited to those which have a resistivity within a range of 10^6 to 10^8 $\Omega\cdot$cm.

When the resistivity of the fine titanium oxide particle is smaller than the above range, the charged amount of the whole toner tends to decrease, thereby causing image failure such as decrease in image density of the image formed.

On the other hand, when the resistivity exceeds the above range, the effect for assisting the movement of electric charges between toner particles is liable to become insufficient and, at the same time, the distribution of the charged amount is widen to generate the highly charged toner, weakly charged toner and inversely charged toner, thereby causing image failure such as toner scattering, fog, etc.

In order to adjust the resistivity of the fine titanium oxide particle within the above range, the kind of a treating agent for imparting a hydrophobicity to the surface of the fine titanium oxide particle may be changed, or the amount of the treating agent to be added may be adjusted. Examples of the treating agent are various coupling agents such as silane, titanate, aluminum and zircoaluminate coupling agents, or silicone oil.

In order to treat the surface of the fine titanium oxide particle with the treating agent, there can be used a dry process comprising adding dropwise or spraying a treating agent alone or a diluted solution thereof while the fine titanium oxide particle is forcibly stirred with a blender, mixing additionally, drying the mixture in an oven, stirring again with a blender and then pulverizing. There can also be used a wet process comprising mixing a fine titanium oxide particle with a treating agent in appropriate organic solution, drying the mixture and then pulverizing.

Further, when the surface of the fine titanium oxide particle is coated with a coated layer of a resin so as to impart a hydrophobicity, the resistivity of the fine titanium oxide particle can also be adjusted by changing the amount of antimony and tin oxide to be added in the coated layer so as to adjust the conductivity.

The particle size of the fine titanium oxide particle of (b) is not specifically limited, but the average particle size of the primary particle thereof is preferably about 10 to 200 nm, more preferably 20 to 100 nm, most preferably 30 to 80 nm, because of the same reason as that of the above fine titanium oxide particle (a).

Further, the amount of the above fine titanium oxide particle to be added is preferably about 0.01 to 10 parts by weight, more preferably 0.05 to 3 parts by weight, most preferably 0.1 to 2 parts by weight, based on 100 parts by weight of the toner particle, because of the same reason as that described above.

The fine titanium oxide particle of the above (c) is limited to those in which an absolute charged amount obtained when it is charged by mixing with a magnetic carrier to be used for charging the toner particle is 5 to 80 μC/g and a charging polarity is the same as that of the toner. That is, in case of fine titanium oxide particle for negatively charged toner, the charged amount is limited within a range of -5 to -80 μC/g. In case of fine titanium oxide particle for positively charged toner, the charged amount is limited within a range of +5 to +80 μC/g.

When the absolute charged amount is smaller than the above range or the charged polarity is contrary to that of the toner, the charged amount of the whole toner is decreased, thereby causing image failure such as decrease in image density of the image formed. On the other hand, when the absolute charged amount exceeds the above range, the charged amount of the whole toner tends to become too large and, at the same time, the distribution of the charged amount is widen to generate the highly charged toner, weakly charged toner and inconversely charged toner, thereby causing image failure such as toner scattering, fog, etc.

The absolute charged amount of the fine titanium oxide particle is preferably 8 to 70 μC/g within the above range, more preferably 10 to 60 μC/g. The charged amount defined herein is not an inherent absolute value of the fine titanium particle, but a relative value which varies depending upon the kind of a magnetic carrier to be used, as described above. That is, there may be used a fine titanium oxide particle wherein the absolute charged amount becomes within the above range when it is charged by mixing with the magnetic carrier to be actually used for charging the toner particle. There can be used a conventional measuring method which has hitherto been known, such as blow off method, for the measurement of the charged amount.

As the method for adjusting the charged amount of the fine titanium oxide particle, there can be suitably employed a method using the fact that the charged amount varies depending upon the resistivity of the fine titanium oxide particle. That is, the resistivity of the fine titanium oxide particle may be adjusted so that the charged amount may be within the above range when it is mixed with the magnetic carrier to be actually used for charging the toner particle.

The particle size of the fine titanium oxide particle of (c) is not specifically limited, but the average particle size of the primary particle thereof may be about 10 to 200 nm, preferably 20 to 100 nm, more preferably 30 to 80 nm, because of the same reason as that of the above fine titanium oxide particle (a).

Further, the amount of the above fine titanium oxide particle to be added is preferably about 0.01 to 10 parts by weight, more preferably 0.05 to 3 parts by weight, most preferably 0.1 to 2 parts by weight, based on 100 parts by weight of the toner particle, because of the same reason as that described above.

Hereinafter, the toner particle to be used in this invention will be explained in detail.

As the toner particle to be used in this invention, there can be used any known toner which has hitherto been used in the dry development process. Such a toner is normally produced by dispersing an additive such as colorant in a fixing resin.

Examples of the fixing resin include styrene polymer, acrylic polymer, styrene-acrylic polymer, olefin polymer (e.g. chlorinated polystyrene, polypropylene, ionomer, etc.), poly(vinyl chloride), polyester, polyamide, polyurethane, epoxy resin, diallyl phthalate resin, silicone resin, ketone resin, poly(vinyl butyral) resin, phenol resin, rosin-modified phenol resin, xylene resin, rosin-modified maleic resin, rosin ester and the like. Among them, the acrylic polymer or styrene-acrylic polymer is preferred in view of ease of pulverization and ease of control of the molecular weight distribution. In case of toner for full color, a polyester having excellent color mixture properties is preferred.

Examples of the colorant to be dispersed in the fixing resin include acetylene black, carbon black, aniline black and the like.

Further, as the colorant for full color, there can be used magenta, cyan and yellow pigments.

Examples of the magenta colorant include C.I. Pigment Red 49, C.I. Pigment Red 57, C.I. Pigment Red 81, C.I. Pigment Red 122, C.I.Solvent Red 19, C.I Solvent Red 49, C.I. Solvent Red 52, C.I. Basic Red 10, C.I. Dispers Red 15, etc., which are classified according to the color index. Among them, quinacridone pigments such as C.I. Pigment Red 122 are suitably used in view of tint of the magenta colorant.

Examples of the cyan colorant include C.I. Pigment Blue 15, C.I. Pigment Blue 16, C.I. Solvent Blue 55, C.I. Solvent Blue 70, C.I. Direct Blue 25, C.I. Direct Blue 86, etc., which are classified according to the color index. Among them, copper phthalocyanine pigments such as C.I. Pigment Blue 15 are suitably used in view of tint of the cyan colorant.

Examples of the yellow colorant include azo pigments such as C.I. Pigment Yellow 1, C.I. Pigment Yellow 5, C.I. Pigment Yellow 12, C.I. Pigment Yellow 15, C.I. Pigment Yellow 17, etc., which are classified with the color index; inorganic pigments such as yellow iron oxide, yellow ocher, etc. Examples of the dye include nitro dyes such as C.I. Acid Yellow 1, etc.; oil-soluble dyes such as C.I. Solvent Yellow 2, C.I. Solvent Yellow 6, C.I. Solvent Yellow 14, C.I. Solvent Yellow 15, C.I. Solvent Yellow 16, C.I. Solvent Yellow 19, C.I. Solvent Yellow 21, etc. Among them, benzidine pigments such as C.I. Pigment Yellow 12 are suitably used in view of tint of the yellow colorant.

An amount of the colorant to be added is preferably 1 to 30 parts by weight, more preferably 2 to 20 parts by weight, based on 100 parts by weight of the fixing resin.

Examples of the typical additive other than colorant include electric charge controlling materials, offset inhibitors and the like.

The electric charge controlling material is blended for controlling friction charging properties of the toner, and classified into two types, i.e. electric charge controlling materials for controlling positive and negative electric charges, according to charging characteristics of the toner.

Examples of the electric charge controlling material for controlling positive electric charge include organic compounds containing a basic nitrogen atom, such as basic dye, aminopyrine, pyrimidine compound, polynuclear polyamino compound, aminosilanes and the like.

Examples of the electric charge controlling material for controlling negative electric charge include oil-soluble dyes [e.g. nigrosine base (C.I. 5045), oil black (C.I. 26150), spiron black, etc.], metal-containing azo pigments, metal naphthenate salts, metal salts of alkyl salicylate, fatty acid soaps, resin acid soaps and the like.

The amount of the electric charge controlling material to be added is preferably 0.1 to 10 parts by weight, more preferably 0.5 to 8 parts by weight, based on 100 parts by weight of the fixing resin.

The offset inhibitor is blended in order to impart the offset inhibition effect to the toner. Examples of the offset inhibitor include aliphatic hydrocarbons, aliphatic metal salts, higher fatty acids, fatty acid esters or a partially saponified material thereof, silicone oil, various wax. Among them, aliphatic hydrocarbons having an weight-average molecular weight of about 1,000 to 10,000 are preferred. For example, low-molecular weight polypropylene, low-molecular weight polyethylene, paraffin wax, low-molecular weight olefin polymer of an olefin unit having 4 or more carbon atoms, silicone oil, etc. may be suitable used alone or in combination thereof.

The amount of the offset inhibitor to be added is preferably 0.1 to 10 parts by weight, more preferably 0.5 to 8 parts by weight, based on 100 parts by weight of the fixing resin.

When a magnetic substance powder is added to the electrophotographic toner of this invention, a magnetic toner as an one-component developer can be obtained.

The magnetic substance is a substance which is strongly magnetized by a magnetic field in the direction thereof. It is preferred that the magnetic substance to be used in this invention is a fine particle having a particle size of not more than 1 μm, particularly about 0.01 to 1 μm, which is chemically stable. Examples of typical magnetic substances include iron oxides such as magnetite, hematite, ferrite, etc.; metals such as iron, cobalt, nickel, etc.; alloys of these metals with aluminium, cobalt, copper, lead, magnesium, tin, zinc, antimony, beryllium, bismuth, cadmium, calcium, manganese, selenium, titanium, tungsten and vanadium; or a mixture thereof.

The amount of the magnetic substance powder to be added is preferably 20 to 300 parts by weight, more preferably 50 to 150 parts by weight, based on 100 parts by weight of the fixing resin.

In addition, various additives such as stabilizers, etc. may be blended in the appropriate amount.

The particle size of the toner particle is not specifically limited in this invention. However, it is preferred to use a small particle size toner having an average particle size of not more than 9 μm, in order to obtain an image having a high image quality, as described above. The average particle size of the small particle size toner is preferably 4 to 9 μm, more preferably 6 to 8 μm, within the above range, in view of the improvement of the image quality.

Incidentally, this invention can also be applied to a normal toner other than the small particle size toner, and therefore the average particle size of the toner particle may exceeds the above range.

The electrophotographic toner of this invention is produced by treating a surface of the toner with the above hydrophobic fine silica particle and fine titanium oxide particle. The surface treatment is conducted by mixing the above respective components in the above amount to be added, followed by mixing with stirring. Thereby, the hydrophobic fine silica particles and titanium oxide can be uniformly adhered on the surface of the respective toner particles. As a mixing apparatus, for example, there can be used various apparatuses which have hitherto been known, such as Henschel mixer, V type mixer and the like.

The hydrophobic fine silica particle and fine titanium oxide particle can also be mixed with the toner particle, simultaneously. However, in order to adhere both fine particles uniformly on the surface of the toner particle, respectively, it is preferred that one fine particle is mixed with the toner particle to adhere on the surface of the toner and, thereafter, the other fine particle is mixed with the above toner particle to adhere on the surface thereof.

The electrophotographic toner thus obtained can be suitably used for a one-component or two-component developer.

When using it as the one-component developer, the electrophotographic toner of this invention, which is obtained by subjecting the toner particle containing the magnetic substance (or no magnetic substance) to the above-described surface treatment, may be used as it is.

On the other hand, in order to obtain the two-component developer, the electrophotographic toner of this invention which was subjected to the above-described surface treatment may be mixed with a carrier.

As the carrier, there can be used glass beads, oxidized or non-oxidized iron powders, magnetic substance particles of ferrite, cobalt, etc., or those of which surface is coated with synthetic resins (e.g. acrylic resin, styreneacrylic resin, fluororesin, silicone resin, polyester resin, etc.) and the like. In normal, such a carrier has an average particle size of 50 to 2000 μm. When using the two-component developer, the concentration of the toner is preferably 2 to 15 % by weight.

EXAMPLES

The following Examples and Comparative Examples further illustrate this invention in detail but are not to be construed to limit the scope thereof.

Example 1 and Comparative Examples 1 to 7

Production of toner particles

100 parts by weight of a polyester resin as the fixing resin, 5 parts by weight of a quinacridone pigment as the colorant and 2 parts by weight of a zinc compound of salicylic acid as the electric charge controlling material for controlling negative electric charge were molten, kneaded, pulverized and classified to produce a toner particle having an average particle size of 8 μm, respectively.

Production of electrophotographic toner

100 parts by weight of the toner particle obtained in the above production of the toner particle was mixed with a hydrophobic fine silica particle shown in Table 1, of which an amount is shown in the same Table 1, with stirring using a Henschel mixer. Further, a fine titanium oxide particle shown in Table 1 was added in an amount shown in the same table and the mixture was stirred to produce a negatively charged electrophotographic toner, respectively.

In Table 1, the symbols shown in the column of "silica" indicate the following hydrophobic fine silica particles, respectively.

I: Hydrophobic fine silica particle treated with hexamethyldisilazane, average particle size of primary particle: 12 nm

II: Hydrophobic fine silica particle treated with dimethyldichlorosilane, average particle size of primary particle: 16 nm

III: Hydrophobic fine silica particle treated with dimethylpolysiloxane, average particle size of primary particle: 16 nm

In Table 1, the symbols shown in the column of the "titanium oxide" indicate the following fine titanium oxide particles, respectively.

i: Fine titanium oxide particle treated with trimethylolpropane, average particle size of primary particle: 50 nm

ii: Fine titanium oxide particle coated with aluminum oxide, average particle size of primary particle: 50 nm iii: Fine titanium oxide particle treated with octyltrimethoxysilane, average particle size of primary particle: 50 nm

The toners obtained in the above respective Examples and Comparative Examples were subjected to the following respective tests, and properties thereof were evaluated, respectively.

Fluidity test

The fluidity of the toners obtained in the above respective Examples and Comparative Examples was measured using an apparatus shown in Fig. **1**.

This apparatus comprises a hopper **1** on which a sample toner is placed, a toner feed roller **2** provided on a bottom opening **11** of the hopper **1**, and a pan **3** provided at the lower position of them. The toner feed roller **2** is a metal cylinder having a diameter of 20 mm, and has the irregularities on the surface thereof. The roller **2** is designed that the sample toner falls on the pan **3** from the hopper **1** when the roller **2** rotates. A predetermined amount of the toner is placed on the hopper **1** and the toner feed roller **2** is allowed to rotate at a predetermined rate to determine the amount of the toner to be fallen on the pan **3** in a predetermined period of time, thereby evaluating the fluidity of the toner. In this measurement, the rotating rate of the toner feed roller **2** was set at 3 rpm to measure the amount of the toner to be fallen on the pan **3** in a period of 5 minutes. The results show that, the more the amount of the toner fallen, the higher the fluidity of the toner is.

Measurement of fog density

Each toner obtained in the above respective Examples and Comparative Examples was mixed with a coating carrier (obtained by coating the surface of a ferrite particle with a styrene-acrylic resin, average particle size: 65 µm) to prepare a two-component developer having a toner concentration of 4 % by weight. An image was formed with the developer 20,000 times, using an electrostatic copying machine (model DC-4585, manufactured by Mita Industrial Co., Ltd.), and the image density of the blank space area of the final image formed was measured using a reflection densitometer (RD-918, manufactured by Macbeth Co.).

Observation of toner scattering

The state of the interior of the copying machine after forming the image 20,000 times was visually judged and evaluated according to the following criteria.

○: No toner scattering

Δ: Slight toner scattering

x: Toner scattering

The results are shown in Table 1.

Table 1

	Silica		Titanium Oxide		Fluidity (Amount to be fallen) [g/5min.]	Fog Density	Toner Scattering
	Kind	Amount (part by weight)	Kind	Amount (part by weight)			
Ex. 1	I	0.5	i	0.7	7.1	0.001	○
Comp. Ex. 1	II	0.5	i	0.7	3.8	0.009	×
Comp. Ex. 2	III	0.5	i	0.7	3.2	0.010	×
Comp. Ex. 3	I	0.5	ii	0.7	6.8	0.009	×
Comp. Ex. 4	I	0.5	iii	0.7	7.5	0.011	×
Comp. Ex. 5	II	1.0	i	0.7	4.7	0.010	×
Comp. Ex. 6	II	0.3	i	0.7	2.8	0.009	△
Comp. Ex. 7	I	0.5	ii	1.0	7.0	0.008	△

As apparent from Table 1, the toner of Example 1 of this invention, which was subjected to the surface treatment using the hydrophobic fine silica particle treated with hexamethyldisilazane and fine titanium oxide particle treated with a polyhydric alcohol (trimethylolpropane), is superior in fluidity, and no image failure (e.g. toner scattering, fog, etc.) generates.

Examples 2 and 3 and Comparative Examples 8 to 12

According to the same manner as that described in Example 1 and Comparative Examples 1 to 7 except for using the fine titanium oxide particle having the resistivity [Ω·cm] shown in Table 2 in an amount shown in the same table, a negatively charged electrophotographic toner was prepared.

The toners obtained in the respective Examples and Comparative Examples were subjected to the above respective tests such as fluidity test, measurement of the fog density and observation of toner scattering, and characteristics thereof were evaluated. The results are shown in Table 2.

Table 2

	Silica		Titanium Oxide		Fluidity (Amount to be fallen) [g/5min.]	Fog Density	Toner Scattering
	Kind	Amount (part by weight)	Resistivity	Amount (part by weight)			
Ex. 2	I	0.5	10^8	0.7	7.1	0.000	○
Ex. 3	I	0.5	10^6	0.7	6.9	0.001	○
Comp. Ex. 8	I	0.5	10^9	0.7	7.2	0.011	×
Comp. Ex. 9	I	0.5	10^5	0.7	7.0	0.010	×
Comp. Ex. 10	II	0.5	10^8	0.7	3.5	0.009	△
Comp. Ex. 11	III	0.5	10^8	0.7	3.1	0.008	△
Comp. Ex. 12	II	1.0	10^8	0.7	4.7	0.010	×

As apparent from Table 2, the toners of Examples 2 and 3, which were subjected to the surface treatment using the hydrophobic fine silica particle treated with hexamethyldisilazane and fine titanium oxide particle having a resistivity of 10^6 to 10^8 Ω·cm, are superior in fluidity, and no image failure (e.g. toner scattering, fog, etc.) generates.

Examples 4 to 6 and Comparative Examples 13 to 16

According to the same manner as that described in Example 1 or Comparative Examples 1 to 7 except for using a fine titanium oxide particle having the charged amount [μC/g] obtained when it is mixed the coating carrier shown in Table 3 in the amount shown in the same table, a negatively charged electrophotographic toner was prepared.

The toners obtained in the respective Examples and Comparative Examples were subjected to the above respective tests such as fluidity test, measurement of the fog density and observation of toner scattering, and properties thereof were evaluated. The results are shown in Table 3.

Table 3

	Silica		Titanium Oxide		Fluidity (Amount to be fallen) [g/5min.]	Fog Density	Toner Scattering
	Kind	Amount (part by weight)	Charged amount	Amount (part by weight)			
Ex. 4	I	0.5	-78	0.7	7.5	0.000	○
Ex. 5	I	0.5	-31	0.7	7.2	0.000	○
Ex. 6	I	0.5	-5	0.7	7.4	0.001	○
Comp. Ex. 13	II	0.5	-31	0.7	3.2	0.008	△
Comp. Ex. 14	III	0.5	-31	0.7	3.3	0.009	△
Comp. Ex. 15	I	0.5	+5	0.7	6.8	0.015	×
Comp. Ex. 16	I	0.5	-100	0.7	7.1	0.012	×

As apparent from Table 3, the toners of Examples 4 to 6, which were subjected to the surface treatment using the hydrophobic fine silica particle treated with hexamethyldisilazane and fine titanium oxide particle wherein an absolute charged amount obtained when it is charged by mixing with a coating carrier to be used for charging the toner particle is 5 to 80 μC/g and a charging polarity is the same as that of the toner, are superior in fluidity, and no image failure (e.g. toner scattering, fog, etc.) generates.

As is described above, the electrophotographic toner of this invention can be superior in fluidity, charging properties and charging stability, because a specific hydrophobic fine silica particle is used in combination with a specific fine titanium oxide particle as an additive for subjecting a toner particle to a surface treatment. Accordingly, the construction of this invention can be suitably used for a small particle size electrophotographic toner for the purpose of attaining a high image quality.

Claims

1. An electrophotographic toner comprising a particulate toner and an additive added to the particulate toner to treat the surface of the particles thereof, the additive comprising hydrophobic fine silica particles treated with hexamethyldisilazane and at least one of the following fine titanium oxide particles:

   (a) fine titanium oxide particles treated with a polyhydric alcohol,

   (b) fine titanium oxide particles having a resistivity of 10^6 to 10^8 Ω.cm, and

   (c) fine titanium oxide particles wherein the absolute charged amount obtained when it is charged by mixing with a magnetic carrier is 5 to 80 μC/g and the charging polarity is the same as that of the toner.

2. An electrophotographic toner comprising a toner particle and an additive to be added to said toner particle to treat a surface of the toner particle, and
   the additive comprising a hydrophobic fine silica particle treated with hexamethyldisilazane and a fine titanium oxide particle treated with a polyhydric alcohol.

3. The electrophotographic toner according to claim 2, wherein the polyhydric alcohol is trimethylolpropane represented by the formula:

$$CH_3\text{-}CH_2\text{-}C(CH_2OH)_3 \qquad (1)$$

   or pentaerythritol represented by the formula:

$$C(CH_2OH)_4 \qquad (2)$$

4. An electrophotographic toner comprising a toner particle and an additive to be added to said toner particle to treat a surface of the toner particle, and
   the additive comprising a hydrophobic fine silica particle treated with hexamethyldisilazane and a fine titanium oxide particle having a resistivity of 10^6 to 10^8 Ω.cm.

5. An electrophotographic toner comprising a toner particle and an additive to be added to said toner particle to treat a surface of the toner particle, and
   the additive comprising a hydrophobic fine silica particle treated with hexamethyldisilazane and a fine titanium oxide particle wherein an absolute charged amount obtained when it is charged by mixing with a magnetic carrier to be used for charging the toner particle is 5 to 80 μC/g and a charging polarity is the same as that of the toner.

6. An electrophotographic toner according to claim 1 or 5, wherein the absolute charged amount is 8 to 70 μC/g.

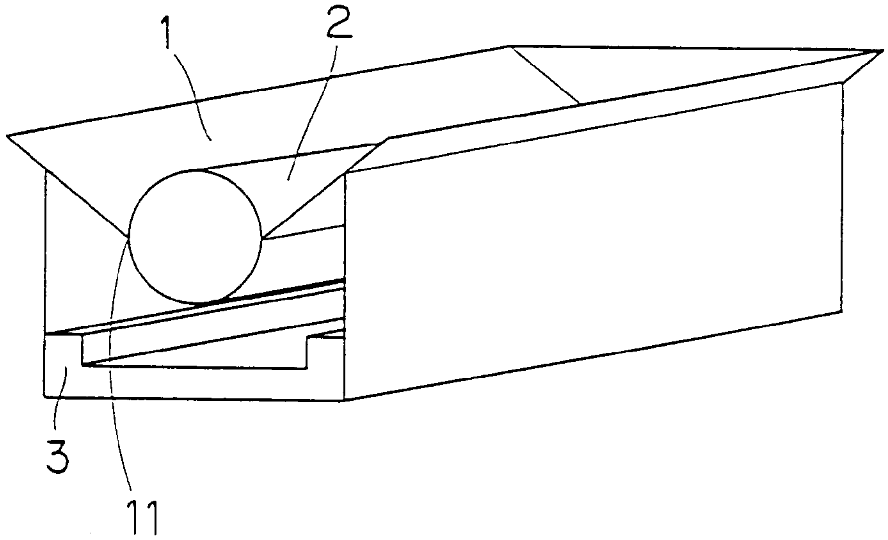
7. An electrophotographic toner according to any preceding claim, wherein the average particle size of the hydrophobic fine silica is 5 to 50 nm.

8. An electrophotographic toner according to any preceding claim, wherein the amount of hydrophobic fine silica is 0.01 to 5 parts by weight, based on 100 parts by weight of the toner particle.

9. An electrophotographic toner according to any preceding claim, wherein the particle size of the fine titanium oxide is 10 to 200 nm.

10. An electrophotographic toner according to any preceding claim, wherein the amount of fine titanium oxide is 0.01 to 10 parts by weight, based on 100 parts by weight of the toner particle.

F I G. 1



European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 30 6186

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	EP-A-0 606 100 (CANON) * page 24 - page 25; tables 2,3A * ---	1,4,5,8,10	G03G9/097
A	EP-A-0 564 002 (CANON) * page 20 - page 21; tables 2, 3A * ---	1,4,5,8,10	
A	US-A-5 272 040 (NAKASAWA ET AL.) * column 10; example 5 * ---	1-10	
A	US-A-4 828 954 (HASHIMOTO ET AL.) * column 6, line 7 - line 51 * -----	1-10	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

G03G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	24 January 1996	Vogt, C

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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