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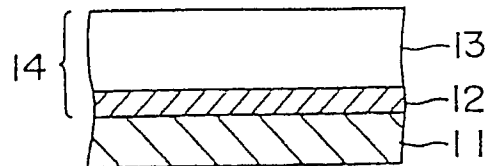
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Developer and image forming process.

A developer for an electrophotographic image forming process comprising a toner which comprises colored particles containing at least a resin and a colorant, and composite particles comprising inorganic particles having an average particle size of 0.01 to 1 μm attached to the surface of resin particles having an average particle-size of 0.1 to 7 μm , the resin of the resin particles having a yield point of between 10 and 500 kg/cm^2 at 20 °C.

Fig. 1



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DEVELOPER AND IMAGE FORMING PROCESS

Field of the Invention

This invention relates to a developer and an image forming process using the developer in which an image is formed by making use of a photoconductive, possibly organic photoreceptor and through the
5 processing steps of forming, developing, transferring and cleaning an electrostatic latent image.

Background of the Invention

In an example of electrophotography, an electrostatic latent image is formed on a photoreceptor by
10 making an electrostatic charge and an exposure to light. The resulting electrostatic latent image is developed with a developer containing a toner so as to form a toner image. Next, the resulting toner image is transferred to a image-transfer member and is then fixed to form a visible image. On the other hand, the toner remaining on the photoreceptor without being transferred to the image transfer member is cleaned up by a cleaning member brought into pressure contact with the surface of the photoreceptor.

15 As the toner constituting a developer applicable to such an image formation process as mentioned above, there has so far been, for example, a proposal for a toner containing colored particles and composite fine particles comprising resin particles surface-treated with inorganic fine particles. -For the details, refer to Japanese Patent Open to Public Inspection, hereinafter referred to as Japanese Patent O.P.I. Publication, No. 64-91143/1986.-

20 In that patent publication, there is a description that, as the resins constituting the resin particles of the composite particles

an acryl type polymer, an acryl*styrene type polymer, the polymers or copolymers of nitrogen-containing addition-polymerizable monomers, the polymers or copolymers of addition-polymerizable carboxylic acids, a fluoro-resin, and a silicone resin, can be utilized.

25 However, when using the above-described toner, in which the resin used as core resin particles of the composite fine particles is hard and fragile, in an image formation process in which such a photoreceptor as an organic photoconductive photoreceptor in particular is used, it was found there arise the following problems:

In the case where, for improving a cleaning operability in a cleaning step, a cleaning member is brought
30 into relatively high pressure-contact with the surface of an organic photoconductive photoreceptor and a cleaning operation is then carried out, the surface of the organic photoconductive photoreceptor is scratched to cause damage thereto, thereby damaging the resin particles constituting the nuclei of the composite fine particles, so that the configurations of the composite fine particles and the surface characteristics thereof are so deteriorated as to cause defective cleaning. Resultingly, there arises the
35 problem that, when forming the next image, the toner particles are made adhered to the plugged inorganic fine particles and are then so fixed as to produce black-specked stains, so-called black-spots, on the resulting image.

40 It is an object of the invention to provide a developer capable of preventing the composite fine particles from forming high-density images stably and repeatedly without producing any black-spot and resulting in cleaning failure.

According to the invention there is provided a developer for an electrophotographic image forming process comprising a toner which comprises colored particles containing at least a resin and a colorant, and composite particles comprising inorganic particles having an average particle size of 0.01 to 1 μm attached to the surface of resin particles having an average particle-size of 0.1 to 7 μm , the resin of the resin
45 particles having a yield point of between 10 and 500 kg/cm^2 at 20° C.

The invention also provides an image forming process comprising cleaning the toner remaining on a photoconductive photoreceptor particularly an organic one, after forming, on the photoreceptor, an electrostatic latent image which is then developed to form a toner image with the developer, and the toner image is transferred to a transfer member, wherein the toner is a toner of the invention.

50 The invention will be better understood from the following description, given by way of example only; with reference to the accompanying drawings, in which:

Figs. 1-6 are each a cross-sectional view illustrating a typical constitutional example of an organic photoreceptor; and Fig. 7 is a schematic illustration of an example of image forming apparatus.

Detailed Description of the Invention

In the invention, as mentioned above, the resin particles capable of functioning as the nuclei of composite fine particles, particularly, those having a yield point within the specific range at a temperature of 20 °C are used. It can, therefore, be realized that the strong resistance and coherence of the resin particles prevents the resin particle from being damaged by the pressure contact force of a cleaning member, so that the cleaning operability can be improved; and it also prevents the surface of an organic photoreceptor from causing a filming phenomenon, so that black-spots can be prevented from being produced by damage on the surface of the photoreceptor.

To be more concrete, the resin particles capable of functioning as the nuclei of the composite fine particles are those capable of yielding, without being damaged, by moderately adapting to a compressive pressure when the pressure is received at an ordinary temperature, and the resin particles have a strong resistance against such a compressive pressure as mentioned above. Therefore, in the case where the remaining toner is to be cleaned up with a cleaning member arranged by bringing it into substantially strong pressure contact with a soft organic photoreceptor, the resin particles are moderately strained to display a cushion function when the particles are sandwiched between the cleaning member and the photoreceptor to receive a strong contact pressure. Therefore, the scratching damage caused by the inorganic fine particles can considerably be reduced, so that the possibility of damaging the resin particles can also be reduced without inducing damage on the organic photoreceptor caused by the inorganic fine particle. Eventually, the images having a sufficient image density and producing no black-spot can be formed stably and repeatedly without producing any fine powder of the inorganic fine particles and the resin particles.

Now, the constitution of the developer of the invention will be detailed. The developer includes coloured particles and composite fine particles.

The composite fine particles in the developer of the invention are those comprising resin particles capable of functioning as the nuclei thereof and having a yield point within the range of 10 to 500 kg/cm² and, preferably, 20 to 300 kg/cm² at a temperature of 20 °C and an average particle-size within the range of 0.1 to 7 μm and, preferably, 0.2 to 5 μm, and inorganic fine particles having an average particle-size within the range of 0.01 to 1 μm and, preferably, 0.01 to 0.5 μm, which are fixed to the surfaces of the resin particles.

Wherein the term, 'yield point', means a value measured in the method specified in JIS K 7113-1981.

The resins having a yield point within the range of 10 to 500 kg/cm² at a temperature of 20 °C are moderately transformed by a compressive pressure at an ordinary temperature and, in addition, they have a resistance which is enough that the resins may not completely be fractured or crushed.

In contrast to the above, if the resin particles has a yield point of less than 10 kg/cm² at a temperature of 20 °C, the resulting resin particles are seriously transformed even by applying a low compressive pressure thereto so that no good rolling function may be displayed by the resulting composite fine particles and the fluidity of the toner is also deteriorated, so that a cleaning is liable to be less good because the adhesion power of the resin particles to an organic photoreceptor is increased.

On the contrary, in case where the yield point of the resins constituting the resin particles exceeds 500 kg/cm² at a temperature of 20 °C, the yieldability of the resins is so lowered that the resin particles may hardly be transformed and may seriously be scratched by inorganic particles when the resin particles receive a strong contact pressure from the cleaning member, therefore, the surface of the organic photoreceptor is liable to damage; and, in addition, the resin particles are rapidly damaged so that a cleaning failure is produced. A fine powder of the resin particles and the inorganic fine particles is also produced on the surface of the organic photoreceptor, which is liable to produce black-spots caused by scratching the surface of the organic photoreceptor.

The average particle-size of the resin particles constituting the composite fine particles is within the range of 0.1 to 7 μm and, preferably, 0.2 to 5 μm. The term, an 'average particle-size', herein means that measured in terms of the volumetric criteria with a laser-diffraction type particle-size analyzer possessing a wet dispersing device, 'Heos' manufactured by Sympatec Co.

When the resin particles have the average particle-size within the above-given range, an excellent rolling function can be displayed by the resin particles, that is to say, an excellent lubricating function can be displayed by interposing the composite fine particles having an suitable particle-size between colored particles. Therefore, the operability of cleaning toner can be improved.

In contrast to the above, when the average particle-size of the resin particles is less than 0.1 μm, the cleaning operability is liable to deteriorate, because the rolling function of the composite fine particles will be insufficient.

On the contrary, when the average particle-size of the resin particles exceeds 7 μm, the image density is liable to be lowered, because the frictional chargeability of the toner is hindered.

The resins constituting the resin particles of the composite fine particles are selected from those having

a yield point within the range of 10 to 500 kg/cm² and, preferably, 20 to 300 kg/cm² at a temperature of 20° C.

Ethylene-vinyl acetate copolymer, polyurethane, vinylidene chloride resin, vinyl chloride resin and ABS resin may typically be used.

5 The average particle-size of the inorganic fine particles constituting the composite fine particles is within the range of 0.01 to 1 μm and, preferably, 0.01 to 0.5 μm. The term, 'an average particle-size of inorganic fine particles', herein means that of the primary particles, that is, an average particle-size measured by observing through a scanning type electron microscope and then analyzing an image in terms of volumetric criteria.

10 When the average particle-size of the inorganic fine particles is within the above-given range, the cleaning operability and sanding functions can be both excellently displayed, so that the portions of the organic photoreceptor affected by deteriorating and filming the surface thereof are removed so as to keep the surface characteristics of the organic photoreceptor stable for a long time.

In contrast to the above, when the average particle-size of the inorganic fine particles is less than 0.01
15 μm, the particles are liable to be embedded in the resin particles, so that the cleaning operability is unsatisfactorily performed. On the contrary, when the average particle-size of the inorganic fine particles exceeds 1 μm, they can hardly be fixed to the surfaces of the resin particles, so that the surface of the organic photoreceptor is liable to be damaged by the isolated inorganic fine particles.

The inorganic materials constituting the inorganic fine particles applicable thereto include, for example,
20 (1) oxides such as silicon oxide, aluminium oxide, titanium oxide, zinc oxide, zirconia oxide, chrome oxide, cerium oxide, tungsten oxide, antimony oxide, copper oxide, tin oxide, tellurium oxide, manganese oxide, boron oxide, barium titanate, aluminium titanate, magnesium titanate, calcium titanate and strontium titanate; (2) carbides such as silicon carbide, tungsten carbide, boron carbide and titanium carbide; and (3) nitrides such as silicon nitride, titanium nitride and boron nitride.

25 The composite fine particles are prepared by fixing the inorganic fine particles to the surface of the resin particles. The expression, 'fixing', does not mean a state where the inorganic fine particles are simply adhered electrostatically to the resin particles, but means a state where the inorganic fine particles are embedded in the resin particles and the length of the embedded portions thereof are each within the range of 5 to 95% of the whole length thereof. The above-mentioned state can be confirmed by observing the
30 surfaces of the composite fine particles through a transmission type or ordinary type electron microscope.

When fixing the inorganic fine particles to the surfaces of the resin particles, it is desired to make the shapes of the resin particles globular and then to fix the inorganic fine particles to the surfaces of the resin particles. The reason thereof is that, when the resin particles are in the globular shape, the inorganic fine particles are uniformly fixed to the inorganic fine particles, so that the isolation of the inorganic fine particles
35 can effectively be prevented. In contrast to the above, when using amorphous resin particles, the inorganic fine particles are fixed non-uniformly to the surfaces of resin particles so that the inorganic fine particles can readily be isolated, and most surfaces of the resin particles are exposed.

The resin particles can be made globe-shaped in the following methods; namely, (1) a method in which the resin particles are fused once by applying heat, and they are then spray-granulated; (2) another method
40 in which the thermally fused resin particles are jet-drawn into water so as to be globe-shaped; and (3) a further method in which globular resin particles are synthesized in a suspension-polymerization process or an emulsion-polymerization process.

The inorganic fine particles can be fixed to the surfaces of the resin particles in the following methods; namely, (1) a method in which the inorganic fine particles and the resin particles are mixed up and the mixture thereof is heated; (2) another method, the so-called a mechanochemical method, in which the
45 inorganic fine particles are mechanically fixed to the surfaces of the resin particles; and so forth. To be more concrete, among the above-mentioned methods applicable thereto include, for example, the following methods; namely, (1) a method in which, after the resin particles and the inorganic fine particles are mixed up with stirring them with a Henschell mixer, a V-type mixer or a turbulent-flow mixer, the inorganic fine
50 particles are electrostatically made adhered to the surfaces of the resin particles and, next, the resin particles having the inorganic fine particles adhered to the surfaces thereof are introduced into a heat-treating apparatus such as a two-pass atomizer or a spray-drier and the surfaces of the resin particles are softened by applying heat, so that the inorganic fine particles are made adhered electrostatically to the surfaces of the resin particles; and (2) another method in which, after the inorganic fine particles are made
55 adhered electrostatically to the surfaces of the resin particles, the former are made fixed to the surfaces of the latter by making use of an apparatus capable of giving a mechanical energy, which is a remodeled impact grinder, such as an Ong mill, a free mill, and a high-bleedizer.

For preparing the composite fine particles, the inorganic fine particles may be compounded into the

resin particles so as to uniformly cover the surfaces of the resin particles. To be more concrete, the inorganic fine particles are usually compounded in a proportion of within the range of 5 to 100% by weight and, preferably, 5 to 60% by weight of the resin particles, though the proportions thereof are varied according to the specific gravity of the inorganic fine particles. If the proportions thereof are within the
5 above-given range, the inorganic fine particles may uniformly be fixed satisfactorily to the surfaces of the resin particles. In contrast to the above, when the proportions of the inorganic fine particles are too low, the cleaning operability is liable to be deteriorated and, when the proportions of the inorganic fine particles are too large, the durability is deteriorated, because the inorganic fine particles are liable to be isolated.

The composite fine particles are added and mixed with colored particles so that the toner is prepared.
10 In that case, the proportion of the composite fine particles to be compounded is desirably within the range of 0.01 to 2.0% by weight to the amount by weight of the colored particles. When the proportions thereof are within the above-given range, an excellent fluidity can be displayed, because the excellent cleaning operability can be displayed and the frictional chargeability of the toner cannot be hindered. In contrast to the above, when the proportions of compounding the composite fine particles are too small, the cleaning
15 operability is liable to be deteriorated. On the contrary, when the proportions of the inorganic fine particles are too large, the image density is liable to be lowered, because the frictional chargeability of the toner is hindered and the fluidity is also deteriorated.

The colored particles constituting the developer of the invention are those containing at least a resin and a colorant.

20 The average particle-size of the colored particles is normally within the range of 1 to 30 μm .

The resins for constituting the colored particles include, for example, a polyester resin, a styrene resin, an acryl resin, a styrene-acryl type copolymer resin, and an epoxy resin.

The colorants for constituting the colored particles include, for example, carbon black, a nigrosine dye, aniline blue, chalcocil blue, chrome yellow, ultramarine blue, DuPont oil red, quinoline yellow, methylene
25 blue chloride, phthalocyanine blue, malachite green oxalate, lump black, and rose bengal.

The colored particles are allowed to contain the other additives, if required, such as a charge controller and a fixability improver.

The charge controllers applicable thereto include, for example, a nigrosine dye. The fixability improvers applicable thereto include, for

30 example, a low molecular weight polyolefin.

When a magnetic toner is to be obtained, magnetic particles are contained, as an additive, in the colored particles. Such magnetic particles applicable thereto include, for example, ferrite and magnetite each having an average particle-size within the range of 0.1 to 2 μm . Such magnetic particles are added usually in a proportion within the range of 20 to 70% by weight of the amount of the colored particles from
35 which the external additives such as the foregoing composite fine particles.

In the invention, inorganic fine particles may further be mixedly added from outside into a mixture of the colored particles and the composite fine particles, thereby constituting a toner. In this way, the fluidity of the toner can be improved by adding the inorganic fine particles thereto. Such inorganic fine particles preferably applicable thereto include, particularly, silica fine particles surface-treated with the agents for
40 making them to be hydrophobic, such as a silane or titanium coupling agent.

An example of the methods for preparing toners each for constituting the developer of the invention will now be detailed. A resin constituting colored particles, a colorant and an additive applicable if required are mixed up together and, the resulting mixture is fusedly kneaded and is then cooled down. After that, the kneaded mixture is pulverized and classified, so that the colored particles have a desired average particle-
45 size. Next, the resulting colored particles and the composite fine particles are mixed up with a Henschel mixer so that the composite fine particles are made electrostatically adhered to the surfaces of the colored particles, thereby preparing the toner.

The developers of the invention may be a binary component type developer comprising carriers mixed in the toner thereof and, if the toner is magnetic, the developers of the invention may also be a single
50 component type developer consisting of only magnetic toner.

From the viewpoint of enhancing the durability of the developer, the so-called coating carriers comprising magnetic particles covered with a resin over the surfaces thereof may preferably be used as the above-mentioned carriers constituting the binary component type developers.

As the magnetic particles, those of ferrite or magnetite may be used.

55 As the covering resins, those of a styrene-acryl type copolymer may be used.

The average particle-size of the carriers is normally within the range of 30 to 150 μm .

The developers of the invention can be applied to the image-forming process including the following processing steps; an electrostatic image is formed on an organic photoreceptor and is then developed with

the developer to form a toner image; the resulting toner image is transferred to a transfer member; and, the toner remaining on the organic photoreceptor is cleaned up.

Now, each of the above-mentioned processing steps will be detailed.

5 -Electrostatic image forming step-

The surface of an organic photoreceptor is uniformly charged by a corona charger and is then exposed imagewise to an optical exposure system, so that an electrostatic image is formed on the organic photoreceptor.

10 The organic photoreceptors are those prepared by laminating, on a conductive support for example, an organic photoreceptive layer comprising an organic photoconductive material dispersively contained in the bonding resins.

Such organic photoreceptors are preferable to have a laminated layer type structure having, particularly, the organic photoreceptive layer comprising a carrier generation layer and a carrier transport layer.

15 The carrier generation layer is a layer containing a carrier generating material capable of adsorbing the rays of visible light to produce a charged carriers. The carrier transport layer is a layer containing a carrier transport material capable of transporting either one or both of the positive or negative carriers having been produced in the carrier generation layer. In the layer laminated type organic photoreceptive layer comprising the above-mentioned carrier generation layer and carrier transport layer, the two basic functions
20 essential for photoreceptive layers, namely, the generation and the transport each of the carriers, can be borne by the layers different from each other. Therefore, the range of selecting the materials applicable to constitute a photoreceptive layer can be widened and, in addition, a material or a material system capable of most suitably performing each of the functions can independently be selected. It can, resultingly, be realized to constitute an organic photoreceptor having the various excellent characteristics required for the
25 image forming process, such as a high surface potential when it is charged, a high charging stability, a high photoreceptivity, and a high stability in repetition use.

The carrier generation materials applicable thereto include, for example, an anthanthrone type pigment, a perylene derivative, a phthalocyanine type pigment, a bisazo type pigment, and an indigoid type dye.

30 The carrier transport materials applicable thereto include, for example, a carbazole derivative, an oxadiazole derivative, a triarylamine derivative, a polyaryllalkane derivative, a hydrazone derivative, a pyrazoline derivative, a stilbene derivative, and a styryltriarylamine derivative.

The thickness of the carrier generation layer is normally within the range of 0.01 to 2 μm , and the thickness of the carrier transport layer is normally within the range of 1 to 30 μm .

35 The bonding resins applicable thereto include, for example, a polycarbonate resin, a vinyl acetate resin, an epoxy resin, a polyurethane resin, a polyester resin, a methacryl resin, an acryl resin, a polyvinyl chloride resin, a polyvinylidene chloride resin, a polystyrene, a polyvinyl acetate, a styrene-butadiene copolymer, a vinylidene chloride-acrylonitrile copolymer, a vinyl chloride-vinyl acetate copolymer, a vinyl chloride--vinyl acetate-maleic anhydride copolymer, a silicone resin, a silicone-alkyd resin, a phenol-formaldehyde resin, a styrene-alkyd resin, and a poly-N-vinyl carbazole.

40 The typical examples of the organic photoreceptors are shown in Figs. 1 through 6.

Figs. 1 through 3 each show an example of organic photoreceptive layer 14 comprising conductive support 11 bearing thereon both of a laminated member consisting of carrier generation layer 12 and carrier transport layer 13.

45 Figs. 2 and 4 each show the other example wherein a further interlayer 15 is interposed between organic photoreceptive layer 14 having the above-mentioned structure and conductive support 11.

Fig. 5 shows an example wherein conductive support 11 is provided thereonto with organic photoreceptive layer 14 which is comprised of carrier generation material 17 dispersively contained in layer 16 containing the carrier transport material as the principal component thereof. Fig. 6 illustrates another example wherein a further interlayer 15 is interposed between the above-mentioned organic photoreceptive
50 layer 14 and conductive support 11.

The conductive supports constituting the organic photoreceptors applicable thereto include, for example, conductively treated by laminating a conductive material such as aluminium, palladium, gold, platinum or indium oxide by a coating, evaporating or laminating means onto the surface of, for example, a metal plate or metal drum comprising aluminium, nickel, copper, zinc, palladium, silver, indium, tin, platinum, gold,
55 stainless steel, steel, brass or the alloy thereof, or an insulating sheet of paper or plastics.

The interlayers are those having the functions to serve as an adhesion layer or a barrier layer, and the constituting materials thereof applicable thereto include, for example, the resins similar to those applicable as the bonding resins for the photoreceptive layer, and the metal oxides such as aluminium oxide and

indium oxide.

-Developing step-

5 In the developing section, an electrostatically charged image having been formed on an organic photoreceptor is developed, upon transporting the developer of the invention by and on developer transport carriers to the developing section.

The developer transport carriers are desirably those having a structure capable of applying a bias voltage. For example, the preferable carriers include those having such a structure as is comprised of a
10 cylindrical sleeve capable of carrying a developer layer on the surface thereof and a magnet having a plurality of magnetic polarities, which is arranged inside the sleeve. The developer layer is transported to the developing section by rotating the sleeve and/or the magnet.

For transporting a uniformly thick developer layer to the developing section, it is desirable to provide a thickness controlling member to the upper stream side of the developing section on the developer transport
15 carrier.

The bias voltage applicable to the developing sleeve may be a DC voltage or a voltage consisting of an AC voltage superimposed on a DC voltage.

-Image transfer step-

20

In this image transfer step, a toner image obtained on an organic photoreceptor in a developing step is transferred onto an image transfer member.

In this image transfer step, an electrostatic image transfer system is preferably used. To be more concrete, for example, an image transfer device capable of generating a DC corona discharge is arranged
25 opposite to an organic photoreceptor through an image transfer member, and a toner having been carried on the surface of the organic photoreceptor is transferred onto the surface of the image transfer member by applying the DC corona discharge to the image transfer member from the rear side of the image transfer member.

30 -Cleaning step-

By making use of a cleaning device comprising a cleaning member such as a cleaning blade brought into pressure contact with an organic photoreceptor, the tone remaining, without being transferred, on the organic photoreceptor is cleaned up.

35 The pressure contact force of the cleaning member with the organic photoreceptor is preferably within the range of 5 to 50 g/cm² from the viewpoint of improving the cleaning operability.

In the initial stage of the cleaning step, it is desirable to add an electrically neutralizing step therein to electrically neutralize the surface of the organic photoreceptor for making the cleaning operability easier. The electrically neutralizing step can be performed with an electric neutralizer capable of generating an AC
40 corona discharge.

-Image fixing step-

45 In this step, a fixed image is formed in such a manner that the transfer member to which a toner image is transferred by a fixing means such as a heat roller type fixing device, in the above-described image transfer step.

Fig. 7 illustrates an example of image forming units capable of performing the above-described image forming steps. In the figure, reference numeral 10 is an organic photoreceptor, 21 is a charger, 22 is an optical exposure system, 23 is a developing device, 24 is an electrically neutralizing lamp, 25 is a transfer
50 electrode, 26 is a separation electrode, 27 is a neutralization electrode, 28 is a cleaning device, 29 is a heat roller type fixing device, 30 is a cleaning blade, and 40 is an original document platen. The image forming unit is of the model in which optical exposure system 22 is fixedly employed and original document platen 40 is movable.

The surface of the organic photoreceptor 10 is uniformly charged by charger 21, and the charged
55 surface thereof is exposed imagewise to optical exposure system 22, so that an electrostatically charged image can be formed on the organic photoreceptor 10 so as to correspond to an original document. The resulting electrostatic image is then developed by developing device 23 so as to form a toner image.

The resulting toner image is electrically neutralized by neutralizing lamp 24 to make it readily

transferred and is then transferred onto transfer paper P. The image transferred transfer paper P is separated from organic photoreceptor 10 by separation electrode 26 and is then fixed by heat roller type fixing device 29, so that a fixed image is formed. On the other hand, organic photoreceptor 10 is electrically neutralized by neutralizing electrode 27 and the toner remaining on organic photoreceptor 10 without being transferred is scratched off by cleaning device 28.

Cleaning blade 30 is comprised of an elastic member made of, for example, a hard urethane rubber having a thickness within the range of 1 to 3 mm, and it has a length substantially corresponding to the width of organic photoreceptor 10 -in Fig. 7, in the vertical direction of the paper surface- and is suspended by a blade holder -not shown-so that the pressure contact position thereof and the pressure contact releasing position are switchable over to each other.

Examples

The examples of the invention and the comparative examples thereto will now be detailed. It is, however, to be understood that the embodiments of the invention shall not be limited thereto. In the following descriptions, the expression, 'part' or 'parts', means a part or parts by weight.

<Resin particles for constituting composite fine particles>

(1) Resin particles A -for the invention-

The particles were those comprising an ethylene-vinyl acetate copolymer -the proportion of ethylene : vinyl acetate = 8 : 2 and having an average particle-size of 3.0 μm at a yield point of 135 kg/cm^2 at 20 °C.

(2) Resin particles B -for the invention-

The particles were those comprising an ethylene-vinyl acetate copolymer -the proportion of ethylene : vinyl acetate = 8 : 2 and having an average particle-size of 0.20 μm at a yield point of 135 kg/cm^2 at 20 °C.

(3) Resin particles C -for the invention-

The particles were those comprising polyurethane and having an average particle-size of 1.0 μm at a yield point of 300 kg/cm^2 at 20 °C.

(4) Resin particles a -for the comparison-

The particles were those comprising an acryl type polymer having no yield point but a property liable to be wrecked and having an average particle-size of 1.0 μm .

(5) Resin particles b -for the comparison-
The particles were those comprising a styrene-acrylonitrile copolymer and having an average particle-size of 0.5 μm at a yield point of 700 kg/cm^2 at 20 °C.

<Inorganic fine particles constituting composite fine particles>

(1) Inorganic fine particles A -for the invention-

The particles were those comprising titanium oxide having an average particle-size of 0.2 μm .

(2) Inorganic fine particles B -for the invention-

The particles were those comprising silicon carbide having an average particle-size of 0.05 μm .

<Preparation of composite fine particles>

The resin particles and the inorganic fine particles each having the combinations and compounded amounts thereof shown in the following Table 1 were sufficiently stirred up with a V type mixer and the inorganic fine particles were made electrostatically adhered to the surfaces of the resin particles. After then, the resulting mixture was put in an improved model of an ordinary type impact pulverizer and was then given an impact, so that composite particles comprising the inorganic fine particles fixed to the surfaces of the resin particles could be prepared.

Under the electron microscopic observation of the surfaces of the resulting composite fine particles and the transmission type electron microscopic observation of the resulting particles, it was proved that the inorganic fine particles were made electrostatically adhered to the surfaces of the resin particles and were brought to the state where they were embedded in the surfaces the resin particles.

Table 1

| | Composite fine particle | Resin particle | | Inorganic fine particle | |
|----|----------------------------|----------------|-------------------|-------------------------|-------------------|
| | | No. | Amount compounded | No. | Amount compounded |
| 5 | A -Invention- | A | 100 parts | A | 30 parts |
| | B -Invention- | B | 100 parts | B | 15 parts |
| 10 | C -Invention- | C | 100 parts | A | 8 parts |
| | a -Comparison- | a | 100 parts | A | 30 parts |
| | b -Comparison- | b | 100 parts | B | 8 parts |
| 15 | <hr/> | | | | |

<Example 1>

20

Polyester resin 100 parts

Carbon black 10 parts

25

Low molecular weight polypropylene 5 parts

The above-given materials were mixed, kneaded, pulverized and classified, so that nonmagnetic colored particles 1 having an average particle-size of 12.0 μm could be obtained.

To the resulting colored particles 1, hydrophobic fine silica particles, 'Aerosil R-972' manufactured by Japan Aerosil Co., and composite fine particles A were added in the proportions of 0.6% by weight and 0.6% by weight, respectively. The resulting mixture was mixed up with a Henschel mixer, so that toner 1 could be prepared.

A mixture was prepared by adding together 5 parts of toner 1 and 95 parts of coating carriers having an average particle-size of 80 μm and comprising ferrite particles whose surfaces were covered with a fluorinated resin -having a proportion of styrene : methyl methacrylate = 3 : 7-, so that a binary component type developer A relating to the invention could be prepared.

40 <Example 2>

Binary component type developer B relating to the invention was prepared in the same manner as in Example 1, except that composite fine particles A were replaced by composite fine particle B in a proportion of 0.3% by weight.

45

<Example 3>

Polyester resin 55 parts

50

Magnetite 40 parts

Low molecular weight polypropylene 3 parts

55

Nigrosine, a charge controller 2 parts

Magnetic colored particles 2 having an average particle-size of 11.0 μm were obtained by processing

the above-given materials in the same manner as in Example 1.

To the resulting colored particles 2, hydrophobic fine silica particles, 'Aerosil R-972' manufactured by Japan Aerosil Co., and composite fine particles B were added in the proportions of 0.4% by weight and 0.4% by weight, respectively. The resulting mixture was mixed up with a Henschel mixer, so that magnetic toner 2 could be prepared. The single component type developer C relating to the invention was so prepared as to consist of magnetic toner 2 only.

<Example 4>

Single component type developer D relating to the invention was prepared in the same manner as in Example 3, except that composite fine particles B were replaced by composite fine particles C in a proportion of 1.2% by weight.

<Comparative example 1>

Binary component type developer a for the comparison use was prepared in the same manner as in Example 3, except that composite fine particles B were replaced by comparative composite fine particles a in a proportion of 0.6% by weight.

<Comparative example 2>

Single component type developer b for the comparison use was prepared in the same manner as in Example 3, except that composite fine particles B were replaced by comparative composite fine particles b in a proportion of 0.4% by weight.

<Preparation of an organic photoreceptor>

According to a construction shown in Fig. 1 organic photoreceptor was prepared in such a way that a double-layered negative charging type photoreceiving layer, which comprises a carrier generating layer containing 4,10-dibromoanthanth-raquinon as a carrier generating substance and a carrier transfer layer containing stylyltriphenyl amine type carrier transferring substance, was laminated on an aluminium electric conductive substrate having a strape of rotating drum. The resulting photoreceptor is hereinafter named organic photoreceptor A.

<Image forming test>

The copied image forming tests were each tried in the following manner. By making use of the developers thus prepared, respectively, an electrostatic latent image formed on an organic photoreceptor was developed, so that a toner image was formed. The toner image was transferred to a transfer member. The transferred toner image was fixed. After the toner image was transferred, an image forming process was carried out, including a cleaning step in which the toner remaining on the organic photoreceptor was cleaned up.

Another copied image forming tests were each tried in the following manner. By making use of developers A, B and a, i.e., the binary component type developers, respectively, and through an electrophotographic copier for binary component type developer use, a modified U-Bix 5000 manufactured by Konica Corp., equipped with the foregoing organic photoreceptor A, a developing device for binary component type developer use, and a cleaning blade, the tests were tried 100,000 times at maximum under the surrounding conditions of a temperature of 20 ° C and a relative humidity of 55%RH.

A further copied image forming tests were each tried in the following manner. By making use of developers C, D and c, i.e., the single component type developers, respectively, and through a trial model of electrophotographic copier for single component type developer use, which was equipped with the foregoing organic photoreceptor A, a non-contact type developing device capable of generating an oscillational electric field in a developing area, and a cleaning blade, the tests were tried 100,000 times at maximum under the surrounding conditions of a temperature of 20 ° C and a relative humidity of 55%RH.

After the above-mentioned tests were tried, the following items were evaluated. The results thereof are shown in Table 2 given below.

(1) Cleaning operability

Immediately after the remaining toners were cleaned up with the cleaning blade in each of the tests, the surface of the organic photoreceptor was visually observed to check up the presence of adhered matters. In the evaluation, it was graded as a mark O when almost none of the adhered matters found; as a mark Δ when some adhered matters found, but they were negligible in the level of practical application; and as a mark X when adhered matters found so many that problems were practically raised, respectively.

(2) Damages on photoreceptor

The surface of the photoreceptor used was visually observed to check up any damages produced. The observations were made after completing the actual copying tests.

(3) Black spot

The resulting copied images were visually observed to check up the presence of black spots caused by the damages on the surface of the organic photoreceptor used. It was graded as a mark O when almost none of black spots found; as a mark Δ when some black spots found, but they are in the practically applicable level; and as a mark X when black spots found so many that the problems are raised in practical application.

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Table 2

| | Developer | Composite fine particle | | Cleaning operability | Damage on photoreceptor | Black spot |
|-----------------------|---------------------------|-------------------------|-----------------------|------------------------|-------------------------|------------------------|
| | | No. | Proportion compounded | | | |
| Inventive Example 1 | A (Binary component type) | A | 0.6 wt% | up to 100,000th copy O | Not produced | up to 100,000th copy O |
| Inventive Example 2 | B (Binary component type) | B | 0.3 wt% | up to 100,000th copy O | Not produced | up to 100,000th copy O |
| Inventive Example 3 | C (Single component type) | B | 0.4 wt% | up to 100,000th copy O | Not produced | up to 100,000th copy O |
| Inventive Example 4 | D (Single component type) | C | 1.2 wt% | up to 100,000th copy O | Not produced | up to 100,000th copy O |
| Comparative Example 1 | a (Binary component type) | a | 0.6 wt% | from the initial stage | Produced | from the initial stage |
| Comparative Example 2 | b (Single component type) | b | 0.4 wt% | from the initial stage | Produced | from the initial stage |

As is obvious from Table 2 shown above, when using any one of developers A through D each of the invention, the surface of an organic photoreceptor could constantly be maintained in excellent conditions and an excellent cleaning operability could also be displayed. In addition, none of black spots could be produced by the damages on the surface of the organic photoreceptor.

In contrast to the above, when using developers a or b each for comparison use, inorganic particles on

surface of the composite fine particles interposed between a cleaning blade and the organic photoreceptor induced damages the surface of the organic photoreceptor at the initial stage because resin particles constituting the composite fine particles were hard, and the cleaning operability was deteriorated.

5 **Claims**

1. A developer for an electrophotographic image forming process comprising a toner, which comprises colored particles containing at least a resin and a colorant, and composite particles, the composite particles comprising inorganic particles having an average particle-size of 0.01 to 1 μm attached to the surfaces of resin particles having an average particle-size of 0.1 to 7 μm , the resin of the resin particles having a yield point of between 10 and 500 kg/cm^2 at 20 °C.
2. The developer of claim 1 wherein the average particle-size of the resin particles of the composite particles is 0.2 to 5 μm .
3. The developer of claim 1 or 2 wherein the yield point of the resin of the composite particles is from 20 to 300 kg/cm^2 at 20 °C.
4. The developer of claim 1, 2 or 3 wherein the resin of the composite particles is ethylene-vinylacetate copolymer, polyurethane resin, vinylidene chloride resin, vinyl chloride resin or ABS resin.
5. The developer of any preceding claim wherein the average particle-size of the inorganic particles is from 0.01 to 0.5 μm .
6. The developer of any preceding claim wherein the inorganic material for the inorganic particles is silicon oxide, aluminium oxide, titanium oxide, zinc oxide, zirconia oxide, chrome oxide, cerium oxide, tungsten oxide, antimony oxide, copper oxide, tin oxide, tellurium oxide, magnesium oxide, boron oxide, barium titanate, aluminium titanate, calcium titanate, strontium titanate, silicon carbide, tungsten carbide, boron carbide, titanium carbide, silicon nitride, titanium nitride or boron nitride.
7. The developer of any preceding claim wherein the weight of the composite particles is 0.01 to 2.0% of the weight of the colored particles.
8. The developer of any preceding claim wherein the developer also comprises a carrier.
9. The developer of any preceding claim wherein the colored particles contain ferrite or magnetite.
10. An image forming process including cleaning a toner remaining on photoreceptor which is preferably organic, forming an electrostatic latent image on the photoreceptor, developing the latent image to form a toner image with the developer, and transferring the toner image to a transfer member; wherein the developer is a developer according to any preceding claim.

Fig. 1

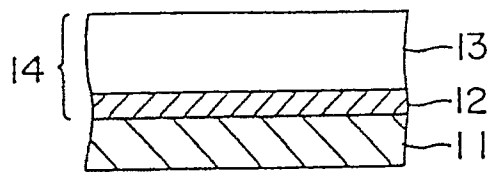


Fig. 2

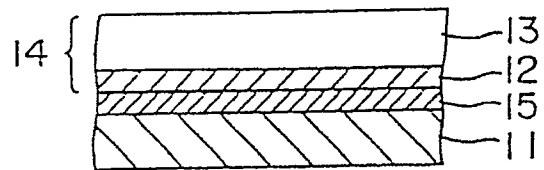


Fig. 3

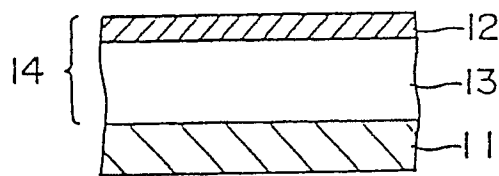


Fig. 4

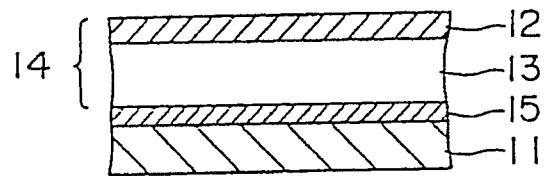


Fig. 5

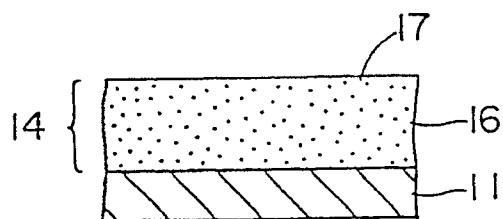


Fig. 6

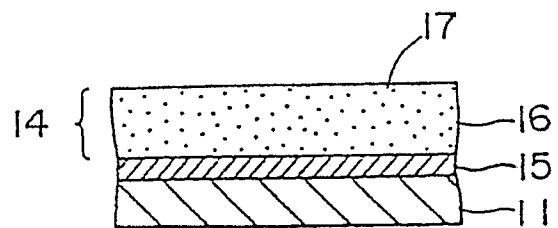


Fig. 7

