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(54) Image forming process.

(57) An image forming process comprising cleaning toner remaining on an amorphous silicon photoreceptor, forming an electrostatic latent image on the amorphous silicon 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 comprises 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 each stuck onto the surfaces of resin particles having an average particle-size of 0.1 to 7 μm and the resin of the resin particle having a yield point from 10 to 500 kg/cm^2 at 20 $^\circ$ C.

Fig. 1

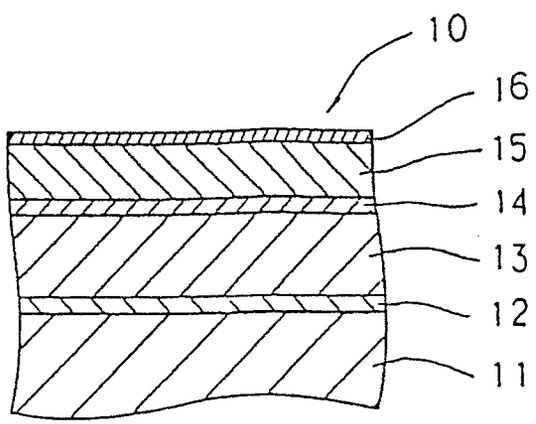

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IMAGE FORMING PROCESS

Field of the Invention

This invention relates to an image forming process utilizing a specific toner in which an image is formed by making use of an amorphous silicon photoreceptor and through the 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 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.

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.-

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 fluororesin, and a silicone resin, can be utilized.

However, when using the above-described toner in an image formation process in which such a photoreceptor as an amorphous silicon photoreceptor in particular is used, it was found there raise the following problems:

(1) In the case where, for improving a cleaning operability in a cleaning step, a cleaning member is brought into relatively high pressure-contact with the surface of an amorphous silicon photoreceptor and a cleaning operation is then carried out, the surface of the amorphous silicon photoreceptor is scratched to cause damage thereto and 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 detriorated as to cause a defective cleaning trouble;

(2) In the case where the resin particles are damaged as mentioned above, the resin particles are reduced to powder and the powder is brought into pressure contact with the surface of the amorphous silicon photoreceptor by the cleaning member. Resultingly, the surface of the photoreceptor is subjected to filming to deteriorate the surface characteristics of the photoreceptor in early stage, so that there arises the problem that the image density is lowered as many images are formed repeatedly; and

(3) In the case where the resin particles are damaged, inorganic fine particles are isolated to produce inorganic fine powder. Also by the inorganic fine powder, the surface of the amorphous silicon photoreceptor is damaged and the damaged portions of the photoreceptor surface are so plugged up as not to be cleaned up. Resultingly, there raises the 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.

According to this invention there is provided an image forming process comprising cleaning toner remaining on an amorphous silicon photoreceptor, forming an electrostatic latent image on the amorphous silicon 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 comprises 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 each stuck onto the surfaces of resin particles having an average particle-size of 0.1 to 7 μm and the resin of the resin particle having a yield point from 10 to 500 kg/cm^2 at 20 $^\circ$ C.

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

Fig. 1 is a cross-sectional view illustrating an typical constitutional example of an a-Si photoreceptor; and Fig. 2 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 a-Si 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 hard a-Si 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. 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 first 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/cm^2 and, preferably, 20 to 300 kg/cm^2 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-sizewithin 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/cm^2 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 has a yield point of less than 10 kg/cm^2 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 a-Si photoreceptor is increased.

On the contrary, in case where the yield point of the resins constituting the resin particles exceeds 500 kg/cm^2 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 a-Si 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 to cause the resulting image density to be lowered by the filming phenomenon produced on the surface of the a-Si photoreceptor, which is liable to produce black-spots caused by scratching the surface of the a-Si 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 dispersion device, 'Helos' 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 composite fine 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, a high density image can be formed, because the operability of cleaning toner can be improved and there is no possibility of hindering the frictional chargeability of the toner.

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/cm^2 and, preferably, 20 to 300 kg/cm^2 at a temperature of 20 °C.

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

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.

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 photoreceptor affected by deteriorating and filming the surface thereof are removed so as to keep the surface characteristics of the 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 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 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, (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.

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 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 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 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 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 tabulent-flow mixer, the inorganic fine 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

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 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 in colored particles so that toner is prepared. 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 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.

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, chalcooil blue, chrome yellow, ultramarine blue, DuPont oil red, quinoline yellow, methylene 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 salicylic acid derivative.

The fixability improvers applicable thereto include, for 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 thereinto 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 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 thereinto. Such inorganic fine particles preferably applicable thereto include, particularly, silica fine particles surface-treated with the agents for 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 the cooled down. After that, the kneaded mixture is pulverized and classified, so that the colored particles having a desired average particle-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 of magnetic, the developers of the invention may also be a single 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.

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 a-Si 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 a-Si photoreceptor is cleaned up.

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

-Electrostatic image forming step-

The surface of an a-Si 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 a-Si photoreceptor.

As the a-Si photoreceptors, a laminated-layer type a-Si photoreceptor in particular may preferably be used. As the surface denaturing layers of the a-Si photoreceptors, it is preferable to use those prepared by introducing a halogen atom X such as a hydrogen and/or fluorine atoms into an a-Si layer and, further, by introducing
a denatured atom Y such as those of a carbon, oxygen or nitrogen atom into a layer chelated with a dangling bond - hereinafter referred to as an a-Si:H(X) layer-.

Such laminated layer type a-Si photoreceptors having the above-mentioned surface denaturing layer are not only non-pollutive but also quite excellent in light resistance, corona-ion resistance, thermal and humid resistance and abrasive resistance.

The reason why they have such an excellent abrasive resistance may be presumed to be larger in the bonding strength of the introduced denatured atom Y to the silicon atom Si than in that of the silicon atom Si to one another.

The physically adhering strength of the toner to the a-Si photoreceptor is reduced because the durface denaturing layer is hard. Therefore, in the transfer step, the toner can readily be transferred from the a-Si photoreceptor to the transfer member, so that the transfer efficiency can be increased. In addition, the amount of the toner remaining on the a-Si photoreceptor without being transferred can be reduced because of the increase in the transfer efficiency, and the cleaning operability can also be improved because the toner can be prevented from being embedded in the surface denaturing layer.

The surface denaturing layer itself has an excellent photoconductivity and raises the dark resistance up to 10^{12} to 10^{13} $\Omega \cdot$cm, -in contrast thereto, an ordinary a-Si:H layer has a dark resistance of 10 ± 8 to 10^{9} $\Omega \cdot$cm-, because the denatured atom Y is introduced thereinto and, resultingly, the electrostatic charge maintenance function of the a-Si photoreceptor can extraordinarily be displayed. The charge • exposure repetition characteristics thereof can also be stable.

The surface denaturing layer can be laminated either on a photoconductive layer directly or on an interlayer arranged onto the photoconductive layer.

The photoconductive layer is also allowed to have a function-separated type layer-arrangement in which the charge generation and charge transport functions are assigned to the separate layers. When using such a multilayered type photoconductive layer arrangement, the surface denaturing layer may be laminated on the outermost layer of the photoconductive layers.

Fig. 1 shows an example of the typical constitution of thea-Si photoreceptors. In the figure, reference numeral 10 is an a-Si photoreceptor. When the charging polarity is positive, the a-Si photoreceptor is constituted by laminating, on a drum-shaped base member 11 made of, for example, aluminium, with P^- type charge blocking layer 12, charge transport layer 13, interlayer 14, charge generation layer 15 and surface denaturing layer 16 in order.

It is desirable that the P^- type charge blocking layer 12 is comprised of an a-Si:C:H(X) layer, an a-Si:C:O:H(X) layer, an a-Si:N:H(X) layer, an a-Si:N:O:H(X) layer, an a-Si:O:H(X) layer or an a-Si:C:O:N:H(X) layer which contains a heavily doped 3A group element, such as those of boron, aluminium and gallium atoms and at least one of the denatured atoms Y such as those of carbon, oxygen and nitrogen atoms. The proportion of the denatured atom Y content is desirably within the range of 0.5 to 40 atm%, and the thickness of charge blocking layer 12 is desirably within the range of 0.01 to 10 μm.

Charge transport layer 13 is desirably comprised of an a-Si:Y:H(X) layer containing a lightly doped 3A group element and at least one of denatured atoms such as those of carbon, oxygen and nitrogen, similar to charge blocking layer 12. The proportion of the denatured atom Y content is desirably within the range of 0.5 to 40 atm%. For improving the charging function and photoreceptivity, it is allowed to introduce boron atoms thereinto so as to make it intrinsic. The thickness of charge transport layer 13 is desirably within the range of 5 to 50 μm and, preferably, the thickness thereof is to be thicker than that of charge generation

layer 15.

Interlayer 14 is to be provided, if required, for enhancing the injection efficiency of carriers. For example, interlayer 14 is desirably comprised of an a-Si:Y:H(X) layer containing at least one of denatured atoms Y such as those of carbon, oxygen and nitrogen atoms. The proportion of the denatured atom Y content is, desirably, smaller than that of charge transport layer 13, preferably, of the order of 1/6 of the contents thereof in charge transport layer 13 and, to be more concrete, within the range of 0.01 to 40 atm%. Interlayer 14 is also desirable to lightly dope a 3A group element therein. The thickness of interlayer 14 is desirably within the range of 0.01 to 2 μm. Interlayer 14 may be of a 2 or more layer laminated member.

Charge generation layer 15 is desirably comprised of an a-Si:H(X) layer into which, if required, a 3A group element is lightly doped. For improving the charging function thereof, it is also allowed to try to make it intrinsice by introducing a boron atoms so as to make the resistivity higher and to improve the mobility of the carriers. The thickness of charge generation layer 15 is desirably within the range of 2 to 15 μm.

Surface denaturing layer 16 is desirably constituted by introducing a halogen atom X such as a hydrogen and/or fluorine atoms into an a-Si layer and by further introducing a denatured atom Y such as those of a carbon, oxygen or nitrogen atom into an a-Si:H(X) layer chelated with a dangling bond. To be more concrete, surface denaturing layer 16 may have various constitution such as an a-Si:C:H(X) layer, an a-Si:C:O:H(X) layer, an a-Si:N:H(X) layer, an a-Si:N:O:H(X) layer, an a-Si:C:N:H(X) layer and an a-Si:C:N:O:H(X) layer.

In surface denaturing layer 16, the proportion of containing denatured atoms Y such as those of carbon, oxygen and nitrogen atoms is desirably within the range of 0.5 to 90 atm%, provided that a total content of silicon atoms and denatured atoms Y is regarded as 100 atm%. When denatured atoms Y are oxygen atoms, the proportion of the content thereof is desirably within the range of 0.5 to 70 atm%. when containing a plurality of denatured atoms Y, such as those of carbon, oxygen and nitrogen atoms, it is advisable to be in the following proportions in terms of atm%; namely, carbon atoms : oxygen atoms : nitrogen atoms = 0~90 : 0.5 ~ 70 : 0 ~ 90. A total proportion of denatured atoms Y is desirably within the range of 0.5 to 90 atm%. The thickness of surface denaturing layer 16 is desirably within the range of 400 Å to 1 μm.

If required, the second interlayer may also be interposed between charge generation layer 15 and surface denaturing layer 16. In the second interlayer, the proportion of the denatured atom Y content thereof is desirably smaller that that of surface denaturing layer 16.

Into the above-described layers constituting a-Si photoreceptor 10, halogen atoms X such as hydrogen atom and/or fluorine atom are desirably introduced.In particular, it is essential to contain hydrogen atoms in charge generation layer 15, for chelating a dangling bond to enhance the photoconductivity and charge stability. To be more concrete, the proportion of hydrogen atom content is desirably within the range of 10 to 30 atm%.

The proportion of the hydrogen atom content can similarly be applied to surface denaturing layer 16, interlayer 14, charge blocking layer 12 and charge transport layer 13. Besides boron for making it to be a P type, the 3A group elements such as aluminium, gallium, indium and tallium may also be used as the impurities for controlling a conductivity mode.

For chelating the dangling bonds in forming each of the layers constituting an a-Si photoreceptor, a halogen atom such as fluorine atom is introduced in the form of SiF_4, in place of or together with hydrogen atoms, so that the layers such as those of a-Si:F, a-Si:H:F, a-Si:C:F, a-Si:C:H:F, a-Si:C:O:F and a-Si:C:O:H:F may be arranged. In this case, the proportion of the fluorine atom content is desirably within the range of 0.5 to 10 stm%.

Each of the layers constituting an a-Si photoreceptor can be prepared in the methods including, for example, a grow discharge decomposition method, a spattering method, an ion plating method, and a method in which silicon is vacuum evaporated in the state where activated or ionized hydrogen is introduced thereinto with a hydrogen discharging tube -for the details, refer to Japanese Patent O.P.I. Publication No. 5678413/1981-.

The above description is made about the case where the charging polarity of a-Si photoreceptor 10 is made to be positive. To make it to be negative, it can be performed by replacing the doping agents, which is to be introduced into each of charge blocking layer 12, charge transport layer 13, interlayer 14, charge generation layer 15 and surface denaturing layer 16, by a 5A group element such as phosphorus, arsenic, antimony and bismuth. In this case, charge blocking layer 12 and interlayer 14 are provided thereto if required and therefore they may be omitted.

Charge transport layer 13 and charge generation layer 15 may be either arranged separately or united into a single layer and, besides, a organic photoconductive layer, a selenium photoconductive layer or a resin dispersion resin type cadmium sulfide or zinc oxide photoconductive layer may also be used for.

Base member 11 may be prepared by using any one of conductive or insulating materials. the conductive materials include, for example, metals such as stainless steel, aluminium, chromium, molybdenum, iridium, tellurium, titanium, platinum, and palladium, or the alloys thereof. The insulating materials include, for example, films made of synthetic resins such as polyester, polyethylene, polycarbonate, cellulose acetate, polypropylene, polyvinyl chloride, polyvinylidene chloride, polystyrene and polyamide, and the sheets, glass plates, ceramics or papers thereof. When using such an insulating material as given above, it is desirable that the surface of the material is conductively treated. To be more concrete, for example, in the case of using a glass plate, the material is to be conductively treated with indium oxide or tin oxide; and, in the case of using a synthetic resin film, a metal such as aluminum, silver, lead, nickel, chromium, molybdenum, iridium, niobium, tantalum, vanadium, titanium and platinum is conductively treated in a vacuum evaporation method, an electron beam evaporation method, or a spattering method, or the insulating material can be conductively treated by laminating the above-given metals.

The forms of base members 11 may be selected from various forms such as a cylindrical, belt, and tabular forms. When forming images continuously at a high speed, an endless belt or cylindrical form may preferably be used. There is no special limitation to the thicknesses of base members 11, but a suitable thickness may be selected from the viewpoints of the manufacturing efficiency, handling convenience and mechanical strength thereof.

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.

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 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 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 genetation 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.

The carrier transport materials applicable thereto include, for example, a carbazole derivative, an oxadiazole derivative, a triarylamine derivative, a polyarylalkane 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.

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.

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.

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 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, 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-

In the developing section, an electrostatically charged image having been formed on an a-Si 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 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, if is desirable to provide a thickness controlling member to the upper stream side of the developing section on the developer transport 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-

In this image transfer step, a toner image obtained on an a-Si 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 opposite to an a-Si photoreceptor through an image transfer member, and a toner having been carried on the surface of the a-Si 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.

-Cleaning step-

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

The pressure contact force of the cleaning member with the a-Si photoreceptor is preferably within the range of 5 to 50 g/cm^2 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 a-Si photoreceptor for making the cleaning operability easier. The electrically neutralizing step can be performed with an electric neutralizer capable of generating an AC corona discharge.

-Image fixing step-

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. 2 illustrates an example of image forming units capable of performing the above-described image forming steps. In the figure, reference numeral 10 is an a-Si 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 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 a-Si photoreceptor 10 is uniformly charged by charger 21, and the charged surface thereof is exposed imagewise to optical exposure system 22, so that an electrostatically charged image can be formed on the a-Si 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 a-Si 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, a-Si photoreceptor 10 is electrically neutralized by neutralizing electrode 27 and the toner remaining on a-Si 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 a-Si photoreceptor 10 -in Fig. 2, 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 $^\circ$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 $^\circ$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 $^\circ$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 $^\circ$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 pulvelizer 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 No.	Amount compounded	Inorganic fine particle No.	Amount compounded
A -Invention-	A	100 parts	A	30 parts
B -Invention-	B	100 parts	B	15 parts
C -Invention-	C	100 parts	A	8 parts
a -Comparison-	a	100 parts	A	30 parts
b -Comparison-	b	100 parts	B	8 parts

<Example 1>

Polyester resin	100 parts
Carbon black	10 parts
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-812' 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 3 parts of toner 1 and 97 parts of coating carriers having an average particle-size of 80 μm and comprising ferrite particles whose surfaces were covered with a styrene-acryl copolymer 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.

<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.

<Example 3>

Polyester resin	55 parts
Magnetite	40 parts
Low molecular weight polypropylene	3 parts
Salicylic acid derivative, 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 0.5% 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 1.0% 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 0.5% by weight.

<Preparation of an a-Si photoreceptor>

An a-Si photoreceptor shown in Fig. 1 was prepared in a grow discharge decomposition method. The details of the preparation are as follows.

After cleaning up the flat and smooth surface of a drum-shaped aluminium base member and then arranging the base member to the inside of a vacuum chamber, the gas was exhausted from the vacuum chamber so as to adjust the gas pressure to be 10^{-8} Torr, and the base member was kept heated at a temperature within the range of 100 to 350 $^{\circ}$ C. Next, highly purified argon gas was introduced, as carrier gas, into the vacuum chamber, and a high frequency electricity having a grequency of 13.56 MHz was applied under the conditions of back pressure of 0.5 Torr. After then, a preliminary discharge was operated.

Next, SiH_4 and CH_4, and reaction gas comprising B_2H_6 were introduced and mixed gas having a flow rate of $Ar:SiH_4:CH_4:B_2H_6 = 1:1:1:1.5\times10^{-3}$ was decomposed by a grow discharging operation. Thereby

laminating to form in order the following three layers on the base member and at a sedimentation rate of 6 μm/hr; namely, a charge blocking layer comprising a P^- type a-Si:C:H layer; a charge transport layer comprising an a-Si:C:H layer -provided, $[B_2H_6]/[SiH_4]$ = 10 ppm by capacity and [C] = 10 atm%-; and an interlayer comprising an a-Si:C:H layer -provided, $[B_2H_6]/[SiH_4]$ = 9 ppm by capacity and [C] = 5 atm%-. The thicknesses of the charge blocking layer, charge transport layer and interlayer were 0.5 μm, 10 μm and 1 μm, respectively.

In succession, the supply of the gasses such as CH_4 was stopped and SiH_4 and B_2H_6 were decomposed by an electric discharging operation, and a charge generation layer comprising a 0.1 μm-thick a-Si:H layer -provided, $[B_2H_6]/[SiH_4]$ = 0.1 ppm by capacity- was laminated on the interlayer.

Next, an a-Si photoreceptor having the constitution shown in Fig. 1 was prepared in the following manner. While introducing denatured gas comprising O_2, CH_4 and N_2 into a vacuum chamber so as to be a flow rate of $O_2:CH_4:N_2$ = 20:60:20, the denatured gas was decomposed by an electric discharging operation, so that a 0.05 μm-thick surface denatured layer was laminated on the charge generation layer. The resulting photoreceptor is hereinafter named a-Si 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 a-Si 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 a-Si 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 a-Si photoreceptor A, a developing device for binary component type developer use, and a cleaning blade, the tests were tried 200,000 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 a-Si 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 200,000 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 a-Si 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 △ 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) Image density

By making use of a Sakura Densitometer manufactured by Konica Corp., the reflective densities were measured. It was graded as a mark O when the reflective density was not lower than 1.25; as a mark △ when it was not lower than 1.1, but less than 1.25; and as a mark X when it was less than 1.1; respectively.

(4) 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 a-Si 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.

Table 2

	Developer	Composite fine particle No.	Composite fine particle Proportion compounded	Cleaning operability	Damage on photoreceptor	Image density	Black spot
Inventive Example 1	A (Binary component type)	A	0.6 wt%	up to 200,000th copy O	Not produced	up to 200,000th copy O	up to 200,000th copy O
Inventive Example 2	B (Binary component type)	B	0.3 wt%	up to 200,000th copy O	Not produced	up to 200,000th copy O	up to 200,000th copy O
Inventive Example 3	C (Single component type)	B	0.5 wt%	up to 200,000th copy O	Not produced	up to 200,000th copy O	up to 200,000th copy O
Inventive Example 4	D (Single component type)	C	1.0 wt%	up to 200,000th copy O	Not produced	up to 200,000th copy O	up to 200,000th copy O
Comparative Example 1	a (Binary component type)	a	0.6 wt%	on 50,000th copy X	Produced	on 70,000th copy X	on 50,000th copy X
Comparative Example 2	b (Single component type)	b	0.5 wt%	on 10,000th copy X	Produced	on 20,000th copy X	on 10,000th copy X

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 a-Si photoreceptor could constantly be maintained in excellent conditions and an excellent cleaning operability could also be displayed. Further, many copied images having both of a high density and a high stability could be reproduced over 200,000 times. In addition, none of black spots could be produced by the damages on the surface of the a-Si photoreceptor.

In contrast to the above, when using developers a or b each for comparison use, composite fine particles interposed between a cleaning blade and the a-Si photoreceptor were wrecked because resin particles constituting the composite fine particles were hard, and the cleaning operability was deteriorated by isolated inorganic fine particles and the fine powder of resin particles, so that the copied image densities were lowered.

Claims

1. An image forming process comprising cleaning toner remaining on an amorphous silicon photoreceptor, forming an electrostatic latent image on the amorphous silicon 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 comprises a toner which comprises colored particles containing at least a resin and a colorant, composite particles the composite particles comprising inorganic particles having an average particle-size of 0.01 to 1 μm each stuck onto the surfaces of resin particles having an average particle-size of 0.1 to 7 μm and the resin of the resin particles having a yield point from 10 to 500 kg/cm^2 at 20 $^\circ$C.

2. The process of claim 1 wherein the average particle-size of the resin particles of the composite particles is 0.2 to 5 μm.

3. The process 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 $^\circ$C.

4. The process of claim 1, 2 or 3 wherein the resin of the composite particles is ethylene-vinylacetate copolymer, polyurethane resin, vinyliden chloride resin, vinyl chloride resin or ABS resin.

5. The process of any preceding claim wherein the average particle-size of the inorganic particles is from 0.01 to 0.5 μm.

6. The process 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, calsium titanate, strontium titanate, silicon carbide, tungusten carbide, boron carbide, titanium carbide, silicon nitride, titanium nitride or boron nitride.

7. The process 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 process of any preceding claim wherein the developer also comprises a carrier.

9. The process of any preceding claim wherein the colored particles contain ferrite or magnetite.

Fig. 1

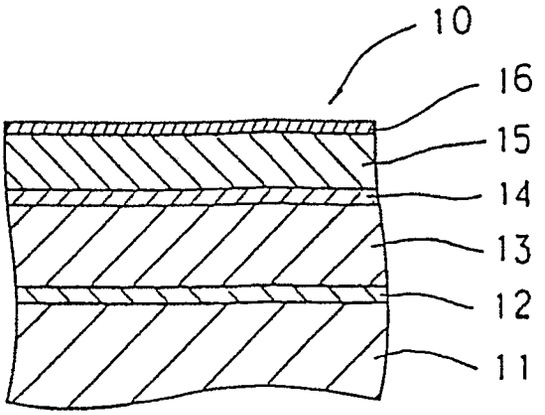

Fig. 2