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(54) Magnetic toner.

(57) An insulative magnetic toner disclosed herein comprises a magnetic powder, a negative charge control agent, a binder resin and a compound having phenazine ring amorphous-silicon photoreceptor.

The magnetic toner according to the invention is effective for preventing the occurrence of picture image blurring under high humidity when used in an amorphous-silicon photoreceptor.

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MAGNETIC TONER

Field of the Invention

The invention relates to a magnetic toner to be used for the development of an electrostatic charge image formed in the electrophotography. More particularly, the invention relates to a magnetic toner which is effective in preventing from occuring a picture image blurring under high humidity when used in an amorphous silicon photoreceptor.

Prior Art

As one of the conventional methods for developing electrostatic charge images, the one-component developing method using the so-called magnetic toner which contains a magnetic fine powder dispersed in a binder resin has been known. This one-component developing method has many advantages as compared with the two-component developing method. For example, it has no need to adjust the toner concentration due to no necessity of using any special carrier and it can use the compact developing system. Therefore, the one-component developing method has been interested in and widely employed.

The magentic toner can be generally classified into two types, i.e. the conductive type and the insulative type. In the case of the conductive magnetic toner, the toner is inducted so as to have the electric charge of a polarity opposite that of the electrostatic charge image and as the result the electrostatic image can be developed. In the successive transferring step, the transfer paper is charged by corona discharge or the like so as to have a polarity opposite that of the toner and as the result the developed image can be transferred to the transfer paper. In this transferring step, the electric charge may penetrate through the transfer paper and hence the polarity of the toner may be changed to lead the lowering of the transfer efficiency. And, the picture image tends to be obtained with signs of blur, stain and unevenness. While, in the case of the insulative magnetic toner having volume resistivity of 10^8 Ω•cm or more, there is no problem such as in the conductive magnetic toner and the picture image of fine qualities can be obtained on the plain paper.

As electrophotographic photoreceptors for the one-component development and tranfer type copying system using the magnetic toner, photoreceptors coated with a dispersion of a fine powder such as CdS or ZnO in organic medium, Se photoreceptor applied the dispersion containig As or Te, formed by vapor-deposition, and organic photoconductors formed of polyvinyl carbazole or trinitrofluorene have been employed.

Recently, the semiconductor properties, particularly the photoconductivity, of the hydrogenated amorphous silicon (hereinafter referred to as "a-Si") have been attracted and the use of the a-Si as the electrophotographic photoreceptor in addition to solar batteries, photosensors and camera tubes has been studied. Although the a-Si is usually prepared in a thin film by the plasma CVD method using silane gas (Si_nH_{2n+2}) as a feed gas, the other processes are proposed for preparing the a-Si which has the properties required in used as the photoreceptor for various applications, such as charged voltage, spectral sensitivity and resistance to repeated copying. For example, diborane, ammonia, oxygen, hydrocarbons, germane (Ge_nH_{2n+2}), silane fluoride or the like is incorporated in the feed gas. Alternatively, multiple layers are deposited on a metallic substrate. See USP 4225222, USP 4265991, USP 4451547, USP 4507375, USP 4471042 and so on.

The a-Si photoreceptor has the improved properties as compared with the conventional photoreceptors since

(1) it is thermally stable (its crystallization temperature is over 400°C while Se photoreceptor has the crystallization temperature of 60°C.);

(2) it has a high and almost constant photosensitivity over visible light wavelength range;

(3) it has high surface hardness (Vickers hardness of over 1500) and shows high resistance to damages such as scratches; and therefore is tried to use in various applications such as plain paper copier, laser printer, facsimile and etc.

However, it has been found that the a-Si photoreceptor has the problem which is not so important in the conventional photoreceptors. That is, the a-Si photoreceptor lacks the stabilities under various environmental conditions, especially under high humidity. When the electrophotography was performed using the a-Si photoreceptor under 70 % of relative humidity, the picture image obtained was not clear and had the blurred outlines. When the electrophotography was performed under higher humidity, no picture image was obtained. These phenomena are totally called as "picture image blurring herein.

Although the causes of the picture image blurring are not completely clarified, it has been confirmed that the picture image blurring becomes more remarkable as the copying operation is repeated. If the photoreceptor is subjected to several

thousands copying cycles (charging - exposure - development - transfer) in the conventional plain paper copier under high humidity, the picture image blurring occurs. It has been also confirmed that the a-Si photoreceptor gives the clear picture image by lowering the humidity even if the picture image blurring occurred under high humidity. For preventing the picture image blurring, therefore, a method of controlling the relative humidity near the surface of the photoreceptor drum constantly below 50 % by always heating the a-Si photoreceptor drum at 40 to 50°C is proposed. However, this method is not satisfactory since it requires to set a heater and a temperature regulating means in the photoreceptor drum, thereby the cost of the copying machine increases and the mechanism of the copying machine complicates.

Background of the Invention

From the results of the experiments carried out for clarifying the causes of the picture image blurring, the inventors obtained the following findings.

(1) Although the phenomenon becomes more remarkable as the copying operation is repeated as described above, this direct cause is to subject the surface of the photoreceptor to the degeneration by corona discharge. This fact has been confirmed from the following experiments.

A commercially available copying machine was modified so as to be subjected to only (a) the cycle of initial corona charge and alternating current corona discharge; (b) the cycle of light irradiation; (c) the cycle of magnetic blush development; or (d) the cycle of cleaning, and was repeatedly subjected to each cycle under normal conditions until 10000 copies was obtained. Thereafter, the copying machine operated under the conditions of 30°C and 85 % of relative humidity (RH). The resultant copies were evaluated with respect to the picture image blurring. As the result, it was found that the picture image blurring occurred only when the a-Si photoreceptor was repeatedly subjected to the corona discharge.

For comparison, a commercially available Se photoreceptor was repeatedly subjected to the corona discharge. Under the same conditions as above, the picture image blurring occurred.

From these facts, it is supposed that in the case of the conventional Se photoreceptor, its surface layer is gradually scraped so as to always keep a fresh surface via the serial copying cycles, particularly development and cleaning cycles due to the relatively low surface hardness, even if the picture image blurring occurred by corona discharging and that in the case of the a-Si photoreceptor, its surface layer degenerated by corona discharging cannot be removed via the developing and/or cleaning cycles due to the very high surface hardness and therefore the degenerated layer accumulates as the copying operation is repeated.

(2) Using the a-Si photoreceptor which occurred the picture image blurring under the conditions of 30°C and 85% of RH after the copying operation was repeated under normal conditions until 10000 copies was obtained, the following experiments were carried out.

By washing the photoreceptor with trichloroethylene or forcedly filming with the fresh toner on the surface of the photoreceptor, the occurrence of the picture image blurring could be prevented.

From the result, it is found that the picture image blurring is caused by the degeneration of the filmy toner and that the picture image blurring cannot occur either by removing the degenerated toner or by filming with a fresh toner.

From the above findings, it is believed that the filmy toner serves as a layer for protecting the a-Si photoreceptor from corona charging and the filmy toner is necessarily refreshed for preventing the picture image blurring. Therefore, the preferable toner should have the high corona resistance and be easily made to be filmy.

Summary of the Invention

An object of the invention is to provide a new electrophotographic method using the a-Si photoreceptor which does not occur any picture image blurring even under high humidity.

Another object of the invention is to provide a new magnetic toner used in the above electrophotographic method.

Another object of the invention is to provide a magnetic toner having the high corona resistance and easily made to be filmy.

Other objects and advantages of the invention will become apparent from the following description.

These objects can be attained by an insulative magnetic toner used in the a-Si photoreceptor according to the invention.

The insulative magnetic toner according to the invention comprises at least a magnetic powder and a negative charge control agent dispersed in a binder resin and further comprises a compound having phenazine ring as an additive which is known as a positive charge control agent added to a positive polarity toner. See USP 2727826, Japanese Patent Application Laying Open Nos. 57-70539, 57-70540, 59-9670, 57-87767, 59-232360, 60-32061 and so on.

Detailed Explanation of the Invention

As the binder resin in the magnetic toner of the invention, various resins known as the binder resin for toner, such as styrene resins, epoxy resins, polyester resins, polyethylene resins can be used. Preferably, the resin having weight-average molecular weight of 1000 to 300000, preferably 2000 to 300000 is used. Particularly, polyester resins is preferable. The polyester resin preferably used comprises as an acid component an aromatic polycarboxylic acid such as phthalic acid, terephthalic acid, isophthalic acid or trimellitic acid or an aliphatic polycarboxylic acid such as succinic acid, fumaric acid, adipic acid or sebacic acid and as an alcohol component an aliphatic polyol such as ethylene glycol, diethylene glycol, propylene glycol, 1,2-propylene glycol or 1,4-cyclohexane diol or an ethylene oxide or propylene oxide adduct of bisphenol A.

As the magnetic powder in the magnetic toner of the invention, various magnetic powder known to be used in the magnetic toner can be used. A metal such as iron, manganese, nickel, cobalt or chromium, an oxide or alloy of the above-mentioned metal such as ferrite represented by MO. Fe_2O_3 ($M=Mn^{2+}$, Ni^{2+}, Cu^{2+}, Mg^{2+} or Zn^{2+}) or magnetite (Fe_3O_4) or a ferromagnetic alloy such as aluminium-manganese alloy or a mixture thereof in a form of finely divided powder can be used. Examples of the commercially available magnetites include MTA-740, EPT-1000, EPT-500 (registrated trade marks) which are produced by TODA KOGYO Corp.;RB-BL, BL-200, BL-250 (registrated trade marks) which are produced TITANIUM KOGYO K.K.) and the like. The magnetic powder of the particle size of 0.1 to 3 micrometers is preferably used.

The content of the magnetic powder in the magnetic toner of the invention is generally 25 to 60 % by weight, preferably 30 to 55 % by weight. If a mixture of the magnetic toners is used, the content of the magnetic powder in each magnetic toner is not necessarily the same.

As the negative charge control agent in the magnetic toner of the invention, various known substances known as the negative charge control agent, such as chlorinated polyolefin, chlorinated polyester, a metal salt of fatty acid or an azo dye complexed with transition metal such as chromium, iron or cobalt can be used. Examples of the commerciallly available negative charge control agent include BONTRON S-31, S-34, E-82 (registrated trade marks) which are produced by ORIENT CHEMICAL INDUSTRIES, LTD. and the like.

The content of the negative charge control agent in the magnetic toner of the invention is generally 0.1 to 10 % by weight, preferably 0.5 to 7 % by weight.

As the essential additive in the magnetic toner of the invention, the compound having phenazine ring such as nigrosine dyes, aniline black dyes, safranine dyes or induline dyes or their modifications with oleic acid, rosine or the like can be used. The nigrosine dye is preferably used. Examples of the commercially available nigrosine dyes include BONTRON N-01, N-03, N-04, N-07, N-09 (registrated trade marks) which are produced by ORIENT CHEMICAL INDUSTRIES, LTD. and the like.

The compound having phenazine ring is internally and/or externally added in the magnetic toner of the invention (the terms "internally addition" and "externally addition" are explained hereinafter). The content of the compound of phenazine ring is varied depending on whether the compound is internally or externally added. When the compound is internally added, its content is generally 0.05 to 30 % by weight, preferably 0.1 to 20 % by weight, more preferably 0.2 to 5 % by weight based on the weight of the binder resin. When the compound is externally added, its content is generally 0.01 to 20 % by weight, preferably 0.05 to 5 % by weight, more preferably 0.1 to 2.0 % by weight based on the weight of the magnetic toner.

As the other additives optionally used in the magnetic toner, an olefinic polymer having the low molecular weight and a finely divided silica powder for improving the fixability and the flowability of the magnetic toner. Alternatively, an electric resistance control agent such as carbon black may be added since it is desirable that the magnetic toner of the invention has the electric resistance of about 10^8 Ω•cm or more, preferably about 10^{14}Ω•cm or more (the above-mentioned electric resistance value is determined by introducing the toner sample in a cylinder with the diameter of 1.6 cm and made of acrylic resin in a height of 0.5 cm, applying the load of 2740g thereto followed by applying the direct voltage of 10000 V/cm to the electrodes on and below the cylinder). Examples of any other additives include the pigment and the like. These additives may be also internally and/or externally added.

The magnetic toner of the invention can be prepared in accordance with any of the known methods such as a kneading method, a spray-drying method or a microcapsulating method. The kneading method is most standard. In the kneading method, the binder resin, the magnetic powder and the negative charge control agent are mixed in a suitable kneader and the resultant mixture is cooled to be solidified and pulverized followed by classify-

ing so as to obtain toner particles having the particle size of about 10 micrometers in which the magnetic powder and the negative charge control agent are dispersed in the binder resin. The compound having phenazine ring and optionally the other additives may be added at this stage. Then, any other additives are added to the resultant toner particles and homogeneously mixed in a suitable mixer so as to obtain the magnetic toner. It is possible to add the compound having phenazine ring at this stage. "Internally addition" means to add at the former stage. " Externally addition" means to add at the latter stage. The compound having phenazine ring and optionally the other additives may be added internally and/or externally.

The thus-prepared magnetic toner of the invention has preferably the average particle size of 5 to 20 micrometers for obtaining the optimum resolving power.

The invention now being generally described, the same will be better understood by reference to certain specific examples which are included herein for purposes of illustration only and are not intended to be limiting of the invention.

Comparative Example

Thirty-six parts by weight of the magnetic powder (magnetite "EPT-1000" (registrated trade mark); produced by TODA KOGYO Corp.), 61 parts by weight of the binder resin (polyester resin "LUNAPAIL 1400" (registrated trade mark); produced by ARAKAWA CHEMICAL INDUSTRIES, LTD.), 1.2 part by weight of the negative charge control agent (chromium-containing azo dye "S-31" (registrated trade mark); produced by ORIENT CHEMICAL INDUSTRIES, LTD.) and 1.8 part by weight of the additive (polypropylene "550P" (registrated trade mark); produced by SANYO CHEMICAL INDUSTRIES, LTD.) were mixed. Then, the mixture was melt-kneaded in the extrusion kneader, cooled to be solidified, roughly pulverized the solidified mixture with the hammer mill and then finely pulverized with the jet mill followed by classifying through the zigzag classifier to obtain the magnetic toner A having the average particle size of 12.2 micrometers.

The thus-obtained toner particles were mixed with 0.5 % by weight of a finely divided silica powder ("R-972" (registrated trade mark); produced by NIPPON AEROGIL K.K.) for improving the flowability of the magnetic toner in the super mixer to obtain a toner sample A.

Example 1

The procedure in Comparative Example was repeated to obtain the magnetic toner B having the average particle size of 10.8 micrometers, provided that 2.0 parts by weight of the compound having phenazine ring (modified nigrosine dye "BONTRON N-04" (registrated trade mark); produced by ORIENT CHEMICAL INDUSTRIES, LTD.) was internally added.

In the same manner as described in Comparative Example, a toner sample B was obtained.

Examples 2 and 3

In these examples, the compounds having phenazine ring were externally added.

The magnetic toner A obtained in comparative Example was mixed with 1 part by weight of the compound having phenazine ring (modified nigrosine dye "BONTRON N-04" (registrated trade mark); produced by ORIENT CHEMICAL INDUSTRIES, LTD.) in the super mixer to obtain the magnetic toner C having the average particle size of 11.8 micrometers (toner sample C).

The magnetic toner A obtained in comparative Example was mixed with 1 part by weight of the compound having phenazine ring (modified nigrosine dye "BONTRON N-03" (registrated trade mark); produced by ORIENT CHEMICAL INDUSTRIES, LTD.) in the super mixer to obtain the magnetic toner D having the average particle size of 12.0 micrometers (toner sample D).

Example 4

After each toner sample had been repeatedly subjected to the copying operation in the copying machine having the a-Si photoreceptor in which the heating system is not provided, the print image was obtaind under the conditions of 30°C and 85% RH. The results are as follows.

When the sample A (Comparative Example) was used, the picture image blurring occurred under high humidity after at most 2,000 copies (A4) were obtained.

When the sample B (Example 1) was used, the clear picture image could be obtained after 50,000 copies (A4) were obtained without occurring the picture image blurring under high humidity.

When the samples C and D (Examples 2 and 3) were used, the clear picture image could be obtained after 500,000 copies (A4) were obtained without occurring the picture image blurring under high humidity.

Effect of the invention

The magnetic toner according to the invention in which the compound having phenazine ring is internally and/or externally added can prevent the occurrence of the picture image blurring in the electrophotography using the a-Si photoreceptor.

The occurrence of the picture image blurring can be prevented using the magnetic toner of the invention even if the photoreceptor is not heated, thereby the cost of the copying machine can be reduced.

The photoconductivity of the photoreceptor can be maintained almost constantly since it is not necessary to heat the photoreceptor by using the magnetic toner of the invention and therefore the clear picture image without showing any little fogging can be obtained.

The constant concentration of the picture image and the improvement of the transfer efficiency (about 10% increase) can be obtained using the magnetic toner of the invention, thereby the consumption amount of the toner can be reduced as well as the photoreceptor and the copying machine can be remarkably prevented from the contamination by the toner.

Claims

1. An insulative magnetic toner used in an amorphous-silicon photoreceptor comprising a magnetic powder, a negative charge control agent, a binder resin and a compound having phenazine ring.

2. The toner according to claim 1, wherein at least the magnetic toner and the negative charge control agent are dispersed in the binder resin.

3. The toner according to claim 1, wherein the compound having phenazine ring are internally and/or externally added.

4. The toner according to claim 3, wherein the compound having phenazine ring is externally added in an amount of 0.01 to 20 % by weight based on the weight of the toner.

5. The toner according to claim 4, wherein the amount of the compound having phenazine ring is 0.05 to 5 % by weight based on the weight of the toner.

6. The toner according to claim 5, wherein the amount of the compound having phenazine ring is 0.1 to 2.0 % by weight based on the weight of the toner.

7. The toner according to claim 3, wherein the compound having phenazine ring is internally added in an amount of 0.05 to 30 % by weight based on the weight of the binder resin.

8. The toner according to claim 7, wherein the amount of the compound having phenazine ring is 0.1 to 20 % by weight based on the weight of the binder resin.

9. The toner according to claim 8, wherein the amount of the compound having phenazine ring is 0.2 to 5 % by weight based on the weight of the binder resin.

10. The toner according to claim 1, wherein the compound having phenazine ring is a nigrosine dye which may be modified.

11. The toner according to claim 1, wherein the content of the magnetic powder is 25 to 60 % by weight.

12. The toner according to claim 11, wherein the content of the magnetic powder is 30 to 55 % by weight.

13. The toner according to claim 1, wherein the magnetic powder is a magnetite.

14. The toner according to claim 1, wherein the content of the negative charge control agent is 0.1 to 10 % by weight.

15. The toner according to claim 14, wherein the content of the negative charge control agent is 0.5 to 7 % by weight.

16. The toner according to claim 1, wherein the negative charge control agent is an azo dye containing the transition metal.

17. The toner according to claim 1, wherein the binder resin is a polyester resin.

18. The toner according to claim 1, which further contains one or more additives.

19. The magnetic toner used in an amorphous-silicon photoreceptor in which 25 to 60 % by weight of a magnetite and 0.1 to 10 % by weight of a chromium-containing azo dye are dispersed in a polyester resin and in which 0.01 to 20 % by weight of a nigrosine dye which may be modified is externally added.

20. The toner according to claim 19, which further contains a polypropylene.

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Re: European Patent Application No. 87 107 293.0
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Case: MCIL-118-2

It is herewith requested to amend the specification as follows:

1. On page 4, line 9, please substitue ""picture image blurring herein"" by the words ""picture image blurring" herein".

2. On page 8, line 1, please correct the Japanese patent application Laying Open No. "57-87767" to correctly read "57-89767".

Respectfully submitted for the applicant.

Dr. N. ter Meer
(European Patent Attorney)