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GB 2046930A
GB 2043932A
GB 2040488A
GB 2038495A
GB 2021794A
GB 1563208
GB 1282017
Schaffert
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(54) **Electrophotographic Developing and Transfer Process**

(57) In an electrophotographic process a magnetic brush development method employs a developer having two types of particles. The particles of one type have a volume resistivity of not less than $10^{13}\Omega\text{cm}$, and the particles of the other type have a volume resistivity of not more than $10^{10}\Omega\text{cm}$. The volume resistivity of this developer will change significantly depending upon the intensity of electric field applied thereto. Thus

during development of a latent image on an electrostatic image bearing photo-conductor the developer is made to have a relatively low resistivity while during the transfer of the developed image to a copy sheet the developer is made to have a relatively high volume resistivity. Residual developer recovered from the photoconductor may be returned to the developing station where particles of one or other of the two types are added to maintain the ratio of the two types of particles at a predetermined level see claims 5 and 6.

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FIG. 1

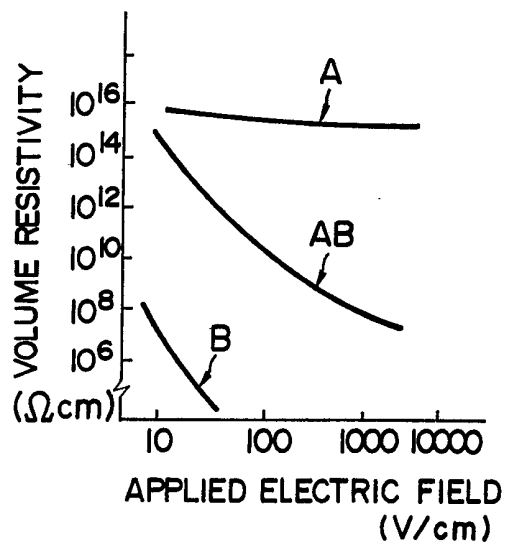


FIG. 2

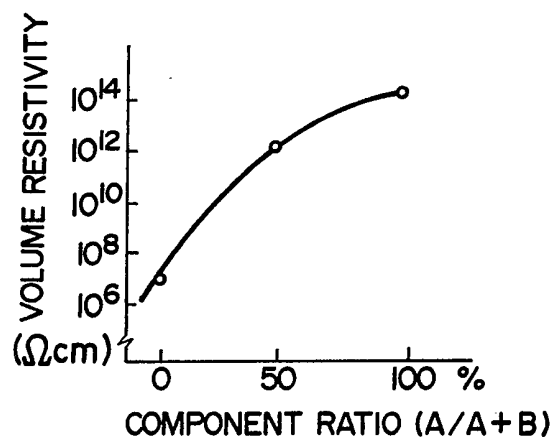


FIG. 3

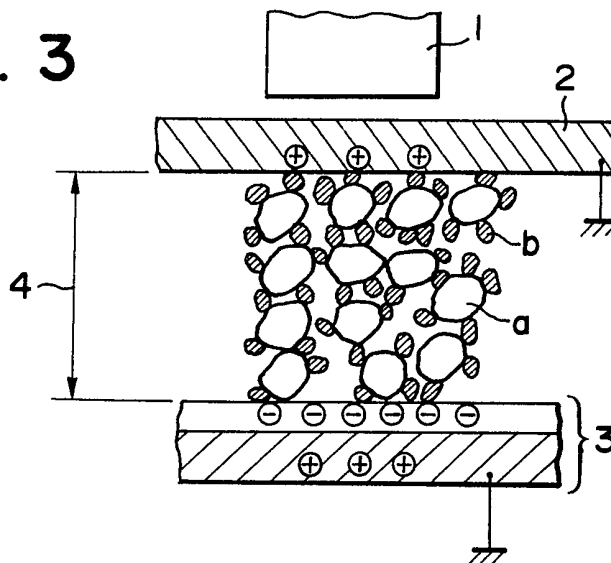


FIG. 4

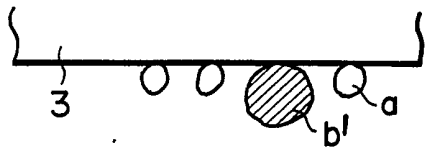


FIG. 6

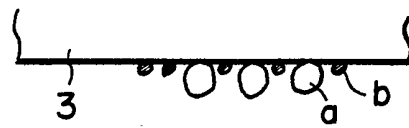


FIG. 5

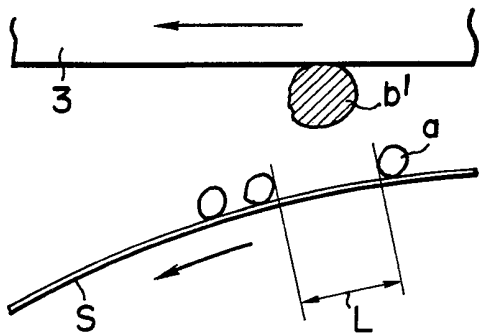


FIG. 7

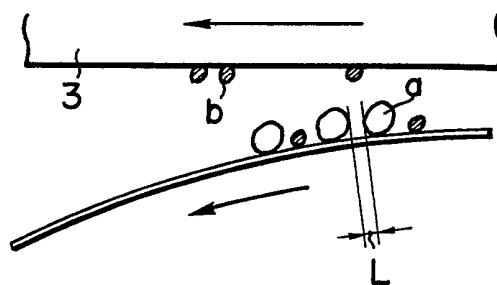


FIG. 8

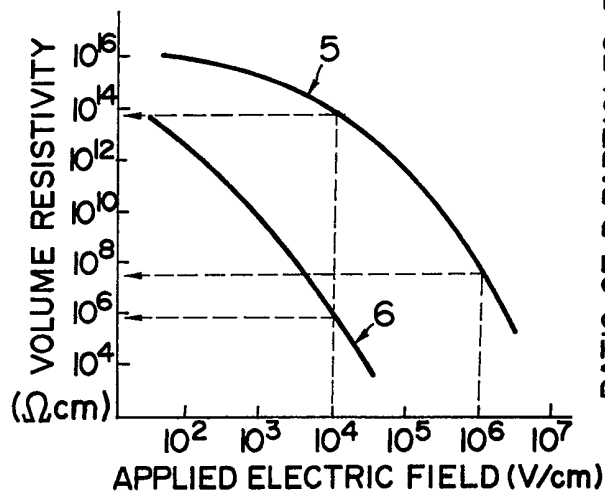


FIG. 9

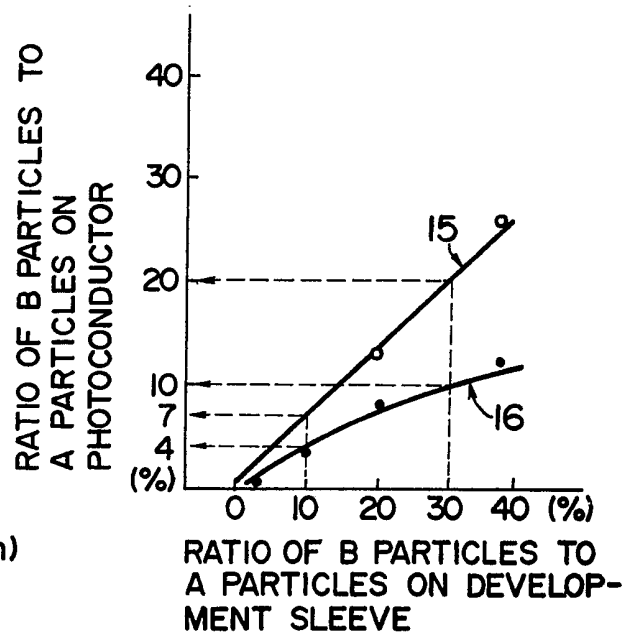


FIG. 10

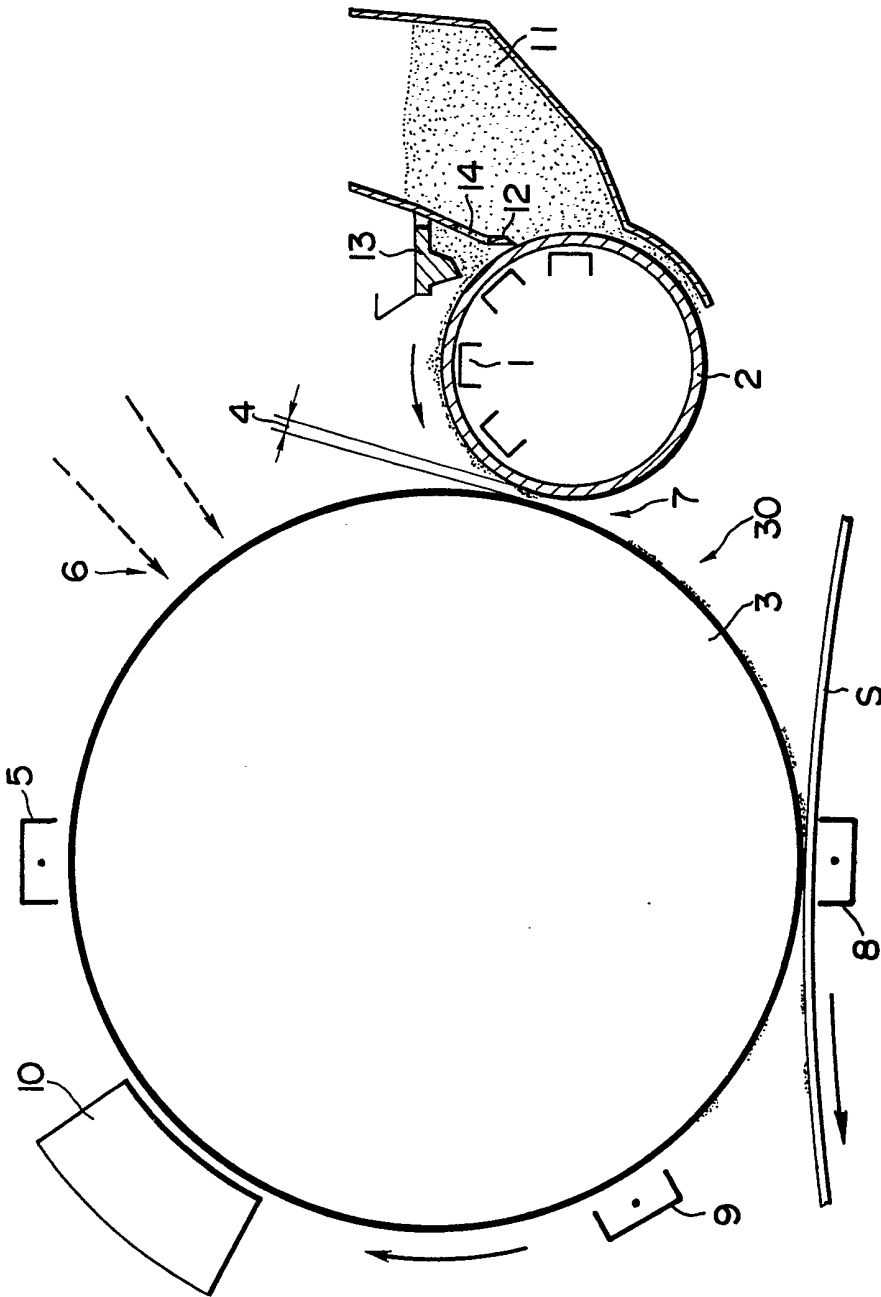
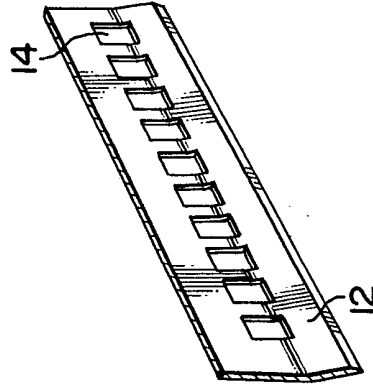


FIG. 11



SPECIFICATION

Electrophotographic Process

The present invention relates to an electrophotographic process.

Conventional electrophotographic processes can be roughly classified into two types of processes in accordance with the types of developers employed, that is, a wet type process employing liquid developers, and a dry type process employing powder developers.

While both types of electrophotographic processes have certain advantages and disadvantages in particular situations, the dry type process is generally considered better than the wet type process and, therefore, more varieties of techniques relating to the dry type electrophotographic process have been studied and developed for practical use.

For instance, there is disclosed a dry type electrophotographic process in Japanese Laid-open Patent Application Serial No. 49-4532/1974, in which a one-component type magnetic toner with the volume resistivity thereof being $10^{11} \Omega \text{ cm}$ or less is employed. In this process, an electrostatic charge pattern, constituting a latent electrostatic image, is formed on the surface of a photoconductor, and that electrostatic charge pattern induces electric charges of a polarity opposite to that of the electrostatic charge pattern in the surface layer of each toner particle deposited on a development sleeve. Due to the electric forces generated by the electric charges induced in the surface layer of the toner particles, the toner particles are attracted to the latent electrostatic image, so that the latent electrostatic image on the photoconductor is developed.

In this electrophotographic process, toner with a relatively low volume resistivity is employed and therefore electric charges are induced on the surface layer of the toner particles in an extremely short time at the time of development and, accordingly, the development efficiency is rather high. In this process, it is necessary that the transfer sheet, to which the developed image is transferred from the surface of the photoconductor, be processed so as to be electrically insulated. Otherwise, electric charges of the toner particles are easily leaked through the paper and development efficiency is decreased and, therefore, the quality of the developed image is significantly degraded. This is in fact what occurs when plain paper with a comparatively low electric volume resistivity is employed.

Alternatively, when the above-mentioned type toner is employed, it is necessary to employ a recording sheet, for instance, a zinc oxide coated sheet. In that process, a latent electrostatic image is directly formed on the recording sheet and that latent electrostatic image is directly developed on the recording sheet with omission of image transfer step.

In order to eliminate the shortcomings of the above-mentioned prior art, there has been

proposed a process which employs a high volume resistivity toner with the volume thereof being $10^{13} \Omega \text{ cm}$ or more. In this process, due to the high volume resistivity of the toner, the image transfer efficiency can be increased and therefore the above-described shortcoming encountered at the time of image transfer can be eliminated. However, at the time of development, due to the high volume resistivity of the toner, sufficient electrostatic charges for development cannot be induced in the surface layer of the toner particles deposited on the development sleeve and, therefore, the latent electrostatic image formed on the surface of the photoconductor cannot be developed with high sharpness, thus decreasing the development efficiency.

This poor development efficiency could be improved to some extent by decreasing drastically the gap between the surface of the photoconductor and the development sleeve, or by injecting additional electric charges into the toner particles during the development step. However, in the method of decreasing the gap between the surface of the photoconductor and the development sleeve, it is extremely difficult to maintain mechanically the small gap with high accuracy, and that method is therefore impractical.

In the method of injecting additional electric charges into the toner particles, uniform charge injection is extremely difficult and that method, too, is not practical.

It is therefore an object of the present invention to provide an electrophotographic process capable of obtaining high quality images by use of plain paper as an image transfer sheet and a developer comprising a mixture of high volume resistivity particles with the volume resistivity thereof being more than $10^{13} \Omega \text{ cm}$ and low volume resistivity particles with the volume resistivity thereof being not more than $10^{10} \Omega \text{ cm}$, preferably less than $10^8 \Omega \text{ cm}$, involving the development of latent electrostatic images formed on a photoconductive element by supplying the developer, attracted in the shape of a brush to a development sleeve with inner magnets, to the latent electrostatic images, and the image transfer of the developed images from the photoconductive element to plain paper.

In the electrophotographic process according to the present invention, the low volume resistivity particles serve as an electrostatic induction promoting agent and the above-mentioned mixture type developer behaves as if it were a developer with low volume resistivity in the development step (where an electric field with a comparatively high intensity is applied thereto) due to the function of the low volume resistivity particles, while in the image transfer step (where an electric field with a comparatively low intensity is applied thereto), the developer behaves as if it were a developer with high volume resistivity. As a result, high development efficiency and high image transfer efficiency can be attained in spite

of the use of plain paper with a comparatively low volume resistivity.

Another object of the present invention is to provide an electrophotographic process of the type described above, particularly capable of maintaining a predetermined optimum quantity ratio of high volume resistivity particles to low volume resistivity particles on the development sleeve throughout the development and image transfer steps, by replenishing either of or both particles as necessary.

According to the present invention, in a development system in which the developer remaining on the photoconductor element is recovered and reused after image transfer, that object is attained by replenishing to a developer tank a developer having the same mixing ratio of the high volume resistivity particles to the low volume resistivity particles as the mixing ratio of the developer transferred to a sheet of transfer paper, while in a development system in which the developer remaining on the photoconductor after development is removed without being recovered, that object is attained by replenishing a developer having the same mixing ratio of the high volume resistivity particles to the low volume resistivity particles as the mixing ratio of the developer deposited on the photoconductor element.

In the drawings,

Fig. 1 shows the relationship between the change in volume resistivity of high volume resistivity particles A and the change in electric field applied thereto; the relationship between the change in volume resistivity of low volume resistivity particles B and the change in electric field applied thereto; and the relationship between the change in volume resistivity of a mixed type developer consisting of the high volume resistivity particles A and the low volume resistivity particles B for use in the present invention and the change in electric field applied thereto.

Fig. 2 shows the relationship between the change in volume resistivity of a mixture of the high volume resistivity particles A and the low volume resistivity particles B and the ratio of the quantity of the particles A to the total quantity of the two particles A and B.

Fig. 3 shows a schematic illustration of the behavior of the high volume resistivity particles and low volume resistivity particles of a mixed type developer during the development step.

Fig. 4 shows a schematic illustration of the deposition state of the high volume resistivity particles a and low volume resistivity particles b' of a mixed type developer on the surface of a photoconductor, in which the particle size of the particles b' is greater than the particle size of the particles a.

Fig. 5 shows a schematic illustration of the deposition state after development of the high volume resistivity particles a and low volume resistivity particles b' (shown in Fig. 4) on a sheet of transfer paper.

Fig. 6 shows a schematic illustration of the deposition state of the high volume resistivity particles a and low volume resistivity particles b of a mixed type developer on the surface of a photoconductor, in which the particle size of the particles b is smaller than the particle size of the particles a.

Fig. 7 shows a schematic illustration of the deposition state after development of the high volume resistivity particles a and low volume resistivity particles b (shown in Fig. 6) on a sheet of transfer paper.

Fig. 8 shows the relationship between the volume resistivity of each of two mixed type developers, each comprising two types of particles with different resistivities and the electric field applied thereto.

Fig. 9 shows the relationship between the quantitative ratio of particles B to particles A on a photoconductor and the quantitative ratio of particle B to particles A on a development sleeve.

Fig. 10 shows a schematic illustration of the main structure of an example of an electrophotographic copying apparatus that can be employed in the present invention.

Fig. 11 shows a perspective view of a scraper of the electrophotographic copying apparatus illustrated in Fig. 10.

First of all, the principle of the present invention will now be explained.

As mentioned previously, in an electrophotographic process in which a latent electrostatic image is formed on the surface of a photoconductor and the latent electrostatic image is developed by a magnetic developer magnetically attracted in the form of a magnetic brush to a development sleeve under application of a comparatively high electric field thereto, and the developed image is transferred from the surface of the photoconductor to a sheet of plain paper under application of a comparatively low electric field thereto, when a developer with low volume resistivity is employed, electric charges are induced on the surface layer of each developer particle, due to the low volume resistivity of the developer, upon the developer particles being supplied to the latent electrostatic image at the time of development. As a result, high development efficiency can be attained.

However, when the developed image is transferred from the surface of the photoconductor to a sheet of plain paper with a comparatively small volume resistivity, the electric charges of the developer particles are easily leaked through the paper and image transfer efficiency is therefore significantly decreased and the quality of the developed image is considerably degraded.

In contrast to this, when a developer with high volume resistivity is employed in the above described electrophotographic process, the image transfer efficiency can be increased due to the high volume resistivity. However, sufficient electrostatic charges for development cannot be induced in the surface layer of the developer

particles deposited on the development sleeve due to the high volume resistivity, and, therefore, the development efficiency is significantly decreased. The result is that the overall image quality obtained is poor.

The above-mentioned facts indicate that it is desirable that a developer for use in the above-mentioned electrophotographic process be comparatively low in volume resistivity at the time of development, while high in volume resistivity at the time of image transfer.

In the present invention, a magnetic toner with the volume resistivity thereof being not less than $10^{13} \Omega \text{ cm}$ is prepared. This magnetic toner with such high volume resistivity is hereinafter referred to as particles A. Furthermore, an electrostatic induction promoting agent with the volume resistivity thereof being not more than $10^{10} \Omega \text{ cm}$ is prepared. This agent with such low volume resistivity is hereinafter referred to as particles B.

These two types of particles A and B are mixed so that a developer with the above-mentioned desired properties is obtained, which behaves as if it were a developer with low resistivity in the development step (where an electric field with a comparatively high intensity is applied thereto), and which behaves as if it were a developer with high resistivity in the image transfer step (where an electric field with a comparatively low intensity is applied thereto).

The following are examples of developers comprising such particles A and B for use in the present invention:—

Example 1

Particles A:

70 parts by weight of Piccolastic D-125 (polystyrene manufactured by Esso Chemical Co., Ltd.) and 30 parts by weight of magnetite were mixed. The mixture was kneaded under application of heat thereto by heat rollers. After cooling the mixture, it was ground to powder and the powder was classified so that particles A with a particle size ranging from $5 \mu\text{m}$ to $30 \mu\text{m}$, with the average particle size being $15 \mu\text{m}$ and with the volume resistivity being $4 \times 10^{15} \Omega \text{ cm}$, were obtained.

Particles B:

As particles B, magnetite, Fe_3O_4 , with a particle size ranging from $1 \mu\text{m}$ to $10 \mu\text{m}$ and with the average particle size being $5 \mu\text{m}$ was employed. The volume resistivity of the particles B was $3 \times 10^7 \Omega \text{ cm}$.

Developer No. 1-1

70 parts by weight of the particles A and 30 parts by weight of the particles B were mixed so that Developer No. 1-1 for use in the present invention was prepared.

How the volume resistivities of particles A, particles B and Developer No. 1-1 are each changed when the intensity of electric field applied thereto is changed was investigated.

The results are shown in Fig. 1. As can be seen

from the figure, the volume resistivity of the particles A was relatively high and was little changed even if the intensity of the electric field applied thereto was changed as indicated by the curve A, whereas the volume resistivity of the particles B was relatively low and was markedly decreased as the intensity of the electric field applied thereto was increased as indicated by the curve B, so that the particles B behaved as if they were substantially electrically conductive particles in a comparatively high electric field range.

In contrast to the volume resistivities of the two particles A and B, the volume resistivity of Developer No. 1-1 comprising the particles A and the particles B was drastically changed in an extremely wide range, depending upon the intensity of the electric field applied thereto as indicated by the curve AB. Specifically, when the intensity of the electric field applied to the developer was relatively small, the volume resistivity of the developer was high, while when the intensity of the electric field applied thereto was great, the volume resistivity of the developer was small.

It is apparent that Developer No. 1-1 behaves as a developer with low resistivity in the development section where a comparatively high electric field is applied thereto, while in the image transfer section where a comparatively low electric field is applied thereto, the developer behaves as a developer with high volume resistivity, thus fulfilling the requirements for the electrophotographic process according to the present invention.

As a matter of course, the volume resistivity of a developer comprising the particles A and particles B will also be changed, depending upon the ratio of the quantity of the particles A to the quantity of the particles B.

Referring to Fig. 2, there is shown the relationship between the change in volume resistivities of the developer consisting of the particles A and the particles B and the ratio in quantity of the particles A in the developer under an electric field ranging from $5 \times 10^3 \text{ V/cm}$ to $1 \times 10^4 \text{ V/cm}$.

As can be seen from Fig. 2, as the ratio of the particles A increases, the volume resistivity of the developer increases.

Developer No. 1-2

90 parts by weight of the particles A and 10 parts by weight of the particles B were mixed so that Developer No. 1-2 for use in the present invention was prepared.

Developer No. 1-3

As particles B, magnetite with the average particle size thereof being $10 \mu\text{m}$ was employed. The volume resistivity of the particles B was $3 \times 10^7 \Omega \text{ cm}$.

70 parts by weight of the particles A and 30 parts by weight of the particles B were mixed so that Developer No. 1-3 for use in the present invention was prepared.

Example 2**Particles A-2**

As the particles A-2, the particles A employed in Developer No. 1-1 were employed.

5 Particles B-2

30 parts of weight of Piccolastic D-125 (polystyrene manufactured by Esso Chemicals Co., Ltd.), 60 parts by weight of magnetite and 10 parts by weight of carbon black were mixed. The mixture was kneaded under application of heat thereto by heat rollers. After cooling the mixture, it was ground to powder and the powder was classified so that particles B-2 with a particle size ranging from 5 to 30 μm , with the average particle size being 10 μm , and with the volume resistivity being $1 \times 10^8 \Omega \text{ cm}$, was obtained.

Developer No. 2-1

50 parts by weight of the particles A-2 and 50 parts by weight of the particles B-2 were mixed so that Developer No. 2-1 for use in the present invention was prepared.

Developer No. 2-2

80 parts by weight of the particles A-2 and 20 parts by weight of the particles B-2 were mixed so that Developer No. 2-2 for use in the present invention was prepared.

EXAMPLE 3**Particles A-3**

34 parts by weight of a styrene-acrylate copolymer (manufactured by Sanyo Chemical Industries, Ltd.), 65 parts by weight of magnetite, and 1 part by weight of Spirit Black SB (a dye manufactured by Orient Chemical Co., Ltd.) were mixed. The mixture was kneaded under application of heat thereto by heat rollers. After cooling the mixture, it was ground to powder and the powder was classified so that particles A-3 with a particle size ranging from 5 to 30 μm , with the average particle size being 20 μm , and with the volume resistivity being $3 \times 10^{14} \Omega \text{ cm}$, were obtained.

Particles B-3

As particles B-3, the particles B-2 employed in Example 2 were employed.

45 Developer No. 3-1

90 parts by weight of the particles A-3 and 10 parts by weight of the particles B-3 were mixed so that Developer No. 3-1 for use in the present invention was prepared.

50 Developer No. 3-2

70 parts by weight of the particles A-3 and 30 parts by weight of the particles B-3 were mixed so that Developer No. 3-2 for use in the present invention was prepared.

55 Example 4**Particles A-4**

50 parts by weight of a styrene-acrylate

copolymer (manufactured by Sanyo Chemical Industries, Ltd.) and 50 parts by weight of magnetite were mixed. The mixture was kneaded under application of heat thereto by heat rollers. After cooling the mixture, it was ground to powder and the powder was classified so that the particles A-4 with the average particle size thereof being 15 μm , and with the volume resistivity thereof being $1 \times 10^{16} \Omega \text{ cm}$, were obtained.

Particles B-4

30 parts by weight of a styrene-acrylate copolymer (manufactured by Sanyo Chemical Industries, Ltd.) and 60 parts by weight of magnetite and 10 parts by weight of carbon black were mixed. The mixture was kneaded under application of heat thereto by heat rollers. After cooling the mixture, it was ground to powder and the powder was classified so that the particles B-4 with the average particle size thereof being 5 μm , and with the volume resistivity thereof being $1 \times 10^{10} \Omega \text{ cm}$, were obtained.

80 Developer No. 4

90 parts by weight of the particles A-4 and 10 parts by weight of the particles B-4 were mixed so that Developer No. 4-1 for use in the present invention was prepared.

85 Example 5**Particles A-5**

The mixture of the same components as in the particles A-4 was kneaded under application of heat thereto by heat rollers. After cooling the mixture, it was ground to powder and the powder was classified so that the particles A-5 with the average particle size thereof being 12 μm , with the volume resistivity thereof being $1 \times 10^{16} \Omega \text{ cm}$, were obtained.

95 Particles B-5

As the particles B-5, the particles B-4 were employed.

Developer No. 5-1

96 parts by weight of the particles A-5 and 4 parts by weight of the particles B-5 were mixed so that Developer No. 5-1 for use in the present invention was prepared.

Developer No. 5-2

93 parts by weight of the particles A-5 and 7 parts by weight of the particles B5 were mixed so that Developer No. 5-2 for use in the present invention was prepared.

The thus prepared Developers Nos. 1-1, 1-2, 1-3, 2-1, 2-2, 3-1, 3-2, 4, 5-1 and 5-2 were found to have the same properties in common as shown in Fig. 1 and therefore are useful for the electrophotographic process according to the present invention. Those examples of developers described are intended to be merely exemplary and a variety of developers for use in the present invention can be made.

A procedure of preparing the high volume resistivity particles (hereinafter collectively referred to as the particles AA) and the low resistivity particles (hereinafter collectively referred to as the particles BB) for use in the present invention will now be summarized in accordance with the experiments conducted by the inventors of the present invention.

The particles AA are prepared by kneading a mixture comprising about 70 to about 35 weight percent of a resinous material, for instance, polystyrene or a styrene-acrylic resin, and about 30 to about 65 weight percent of a magnetic material, for instance, magnetite (Fe_3O_4), and a dye when necessary, under application of heat thereto, and grinding the mixture to powder with a particle size ranging from $5\ \mu\text{m}$ to $30\ \mu\text{m}$ and with the average particle size thereof being in the range from $10\ \mu\text{m}$, to $20\ \mu\text{m}$; whereas the particles BB are prepared by pulverizing only a magnetic material, for instance, magnetite, to particles with a particle size ranging from $1\ \mu\text{m}$ to $10\ \mu\text{m}$ and with the average particle size thereof being in the range of $5\ \mu\text{m}$ to $6\ \mu\text{m}$, or by kneading a mixture comprising about 30 weight percent of a resinous material, for instance, a styrene-acrylic resin, about 60 weight percent of a magnetic material, for instance, magnetite, and about 10 weight percent of carbon black under application of heat thereto and grinding the mixture to powder with the average particle size thereof being in the range of $1/5$ to $1/2$ the average particle size of the particles AA and the volume resistivity thereof being not more than $10^{10}\ \Omega\ \text{cm}$, preferably less than $1 \times 10^8\ \Omega\ \text{cm}$.

When only the magnetic material is used as the particles BB, 90 to 70 weight percent of the particles AA is mixed with 10 to 30 weight percent of the particles BB, while when a ground mixture of the resinous material, the magnetic material and carbon black is employed, 80 to 50 weight percent of the particles AA is mixed with 20 to 50 weight percent of the particles BB, whereby a mixed type developer for use in the present invention can be prepared.

Referring to Fig. 3, the development mechanism of the electrophotographic process according to the present invention, and the reason the developers described for use in the present invention work well, will now be more specifically explained.

In the figure, reference numeral 1 indicates a stationary inner magnet disposed within a development sleeve 2 which rotates around the stationary inner magnet 1 and is grounded. Reference numeral 3 indicates a photoconductive layer which is also grounded. Reference numeral 4 indicates the development gap between the development sleeve 2 and the photoconductive layer 3. In the present invention, it is preferable that the development gap 4 be less than 1 mm, more preferably in the range of 0.1 mm to 0.5 mm.

In the development gap 4, the particles A represented by reference symbol a and the

particles B represented by reference symbol b are positioned in such a manner that the particles b cover the surface of each of the particles a.

Furthermore, in this development section, development of latent electrostatic images formed on the surface of the photoconductive layer 3 is performed by electrostatic induction under application of a relatively high electric field and the particles b serve to promote such electrostatic induction for the development.

For development by electrostatic induction, it is preferable that the developer positioned in the development gap 4 be low in volume resistivity, that is, electrically conductive as mentioned previously.

On the other hand, after the development, it is necessary that the electric charges of the developer particles be maintained as high as possible until the developed images are transferred from the surface of the photoconductor to a sheet of image transfer paper. In other words, the volume resistivity of the developer particles must be high enough to retain the electric charges. Specifically, it must be not less than $10^{13}\ \Omega\ \text{cm}$. In particular, if the volume resistivity of the developer particles is less than $10^{13}\ \Omega\ \text{cm}$, electric charges of the developer particles are easily leaked out when the developed image is transferred from the surface of the photoconductor to the transfer paper, and therefore image transfer efficiency is significantly decreased.

When the potential of the first charges applied to the photoconductor is 1000 V and the development gap 4 is 1 mm, the electric field applied to the developer particles at the time of development is approximately $10^4\ \text{V/cm}$. When a developer consisting of only the particles A is employed under the electric field of $10^4\ \text{V/cm}$, its volume resistivity is as high as $10^{14}\ \Omega\ \text{cm}$, which can be seen from the relationship between the volume resistivity of the developer and the electric field applied thereto is shown by curve 5 in Fig. 8. When the volume resistivity of the developer is as high as $10^{14}\ \Omega\ \text{cm}$, image development by electrostatic induction cannot be performed at all. For successful image development by electrostatic induction under the above-mentioned conditions, it is necessary that the volume resistivity of the developer particles be not more than $10^8\ \Omega\ \text{cm}$ under the electric field of $10^4\ \text{V/cm}$.

The relationship between the volume resistivity of the previously mentioned Developer No. 1-1 consisting of 70 parts by weight of the particles A and 30 parts by weight of the particles B and the electric field applied thereto is shown by a curve 6 in Fig. 8. As can be seen from the curve 6, the particles B serve to promote electrostatic induction in the developer and the volume resistivity of the developer is less than $10^6\ \Omega\ \text{cm}$ under the electric field of $10^4\ \text{V/cm}$. Electrostatic induction sufficient for image development can be caused to occur at a volume resistivity less than $10^6\ \Omega\ \text{cm}$.

The exact mechanism of the functioning of the particles B as an electrostatic induction promoting agent is unknown. Probably it is in that the particles B work as electrodes. Suppose the diameter of each particle B is $10\ \mu\text{m}$ and the potential of the electric charges applied to the photoconductor is 1000 V, the electric field applied to each particle B is substantially $10^6\ \text{V/cm}$ and consequently it is supposed that the overall volume resistivity of the developer is not more than $10^8\ \Omega\ \text{cm}$.

In the present invention, the ratio of the particle size of the particles A to the particle size of the particles B is an important factor.

As described previously, the particle size of the particles A is greater than the particle size of the particles B. The reason for this will now be explained in detail.

When the particle size of the particles B is greater than that of the particles A, the particles A (indicated by a in Fig. 4) and particles B (indicated by b' in Fig. 4) are distributed on the surface of a photoconductive layer 3 as shown in Fig. 4. Microscopically, comparatively large particles b' are distributed from place to place like rocks in the desert of particles a. When a developed image made of the particles a and particles b' is transferred from the surface of the photoconductive layer 3 to a sheet of transfer paper, not all the particles b' with a comparatively low volume resistivity are transferred from the surface of the photoconductive layer 3, but some of them remain on the photoconductive layer 3. The result is that the image transferred to the transfer paper has conspicuously untransferred portions from place to place corresponding to the untransferred particles b' with a comparatively large diameter as shown in Fig. 5.

When the particle size of the particles B is smaller than that of the particles A, they are distributed on the photoconductive layer 3 as illustrated in Fig. 6, where the particles A are indicated by a and particles B are indicated by b. The smaller size of the particles b does not make any difference in image transfer efficiency. However, when the developed image is transferred to a sheet of transfer paper, untransferred particles b are much less conspicuous on the transfer sheet as shown in Fig. 7 than in the case shown in Fig. 5, as is apparent from the comparison of the untransferred gaps L on both sheets of transfer paper. For better image quality, it is thus necessary that the particles B be smaller in size than the particles A.

In the electrophotographic process according to the present invention, the quantitative ratio of the particles A to the particles B in the developer is very important to achieve the object of the present invention.

However, as discussed so far, due to the difference in volume resistivity between the particles A and the particles B, the transfer rates of the two types of the particles from the photoconductive layer to sheets of transfer paper

are not the same and, therefore, in the course of multiple copying, the mixing ratio of the particles A to particles B in the developer deposited on the development sleeve gradually changes.

In particular, in a copying system where residual developer on the photoconductor is recovered and is returned to a developer tank, the percentage of the particles B increases over time since their transfer efficiency is smaller than the transfer efficiency of the particles A.

Yet, in this process, it is an indispensable requirement that the mixing ratio of the particles A to the particles B be substantially constant or be in a predetermined appropriate range.

In order to fulfil that requirement, a method of controlling separately the quantity of the particles A and the quantity of the particles B, to be replenished in the developer per unit time, by detecting momentarily the mixing ratio of the particles A to the particles B deposited on the development sleeve seems possible. However, this method is not practical.

The inventors of the present invention discovered that the following two developer replenishment methods are effective for use in the present invention:

The first method is for a development system in which the developer remaining on the photoconductor after image transfer is recovered and reused. In this method, a developer having the same mixing ratio of the particles A to the particles B as the mixing ratio of the particles A to the particles B in the developer transferred to a sheet of transfer paper is replenished to a developer tank, whereby the originally predetermined mixing ratio of the particles A to the particles B on the development sleeve can be maintained.

The second method is for a development system in which the developer remaining on the photoconductor after image transfer is removed, but not recovered for reuse. In this method, a developer having the same mixing ratio of the particles A to the particles B as the mixing ratio of the particles A to the particles B in the developer deposited on the photoconductor in the form of a toner image is replenished to a developer tank, whereby the originally predetermined mixing ratio of the particles A to the particles B on the development sleeve can be maintained.

Referring to Fig. 10, a development apparatus for use in the present invention will now be explained. In the figure, around a photoconductor drum 30 there are arranged in the direction of the rotation of the photoconductor drum 30, a charger 5 for performing the first charging of the photoconductor drum 30, an exposure section 6, a development section 7, a charger 8 for image transfer, a charger 9 for quenching electric charges on the photoconductor drum 30 and a cleaning apparatus 10.

In an upper side position of a development sleeve 2, which position is opposite to the development section 7 with respect to the development sleeve 2, there is disposed a

developer replenishing tank 11. Furthermore, there are disposed a scraper 12 and a doctor blade 13 around the development sleeve 2 in the rotation direction thereof.

5 The scraper 12 is disposed in such a manner that its top edge portion is in elastic contact with the peripheral surface of the development sleeve 2, and has a number of small windows 14.

10 The doctor blade 13 is disposed in such a manner that its top edge portion is slightly away from the peripheral surface of the development sleeve 2.

The developer consisting of the particles A and particles B is attracted to the peripheral surface of the development sleeve 2 by the magnetic attraction of stationary inner magnets 1 disposed within the development sleeve 2, and is transported to the scraper 12 as the development sleeve 2 is rotated. The developer attracted to the development sleeve 2 is scraped off the surface of the development sleeve 2 by the scraper 12 and is mixed well at the same time. The well mixed developer passes through the small windows 14 and is then transported to the doctor blade 13, where the developer attracted, in the form of a brush, to the development sleeve 2 is regulated to a predetermined thickness and is then supplied to the development section 7 in accordance with the rotation of the development sleeve 2. The developer is thus transferred from the development sleeve 2 to the surface of the photoconductor drum 30, so that a latent electrostatic image formed on the surface of the photoconductor drum 30 is developed. The developed image is then transferred from the surface of the photoconductor drum 30 to a sheet of transfer paper S in the image transfer section with the charger 8 for image transfer disposed therein.

40 In the development system in which developer remaining on the photoconductor after image transfer is removed, without recovering the same, the residual developer on the photoconductor drum 30 is removed by the cleaning apparatus 10.

45 In contrast to this, in the development system in which developer remaining on the photoconductor after image transfer is recovered and reused, the cleaning apparatus 10 is not disposed; rather, the residual developer on the photoconductor drum 30 is attracted to the peripheral surface of the development sleeve 2, so that the photoconductor drum 30 is cleaned. Therefore, in the latter development system, 55 image development and image transfer are performed during the first revolution of the photoconductor drum 30 and the cleaning of the photoconductor drum 30 is performed during the second revolution of the photoconductor drum 30. In other words, this system is of the so-called one-copy-per-two-revolutions type.

60 Referring to Fig. 9, there is shown the relationship between (1) the variation in the ratio of the particles B in the developer consisting of the particles A and the particles B deposited on

the development sleeve 2 and (2) the variation in the ratio of the particles B in the developer transferred to the surface of the photoconductor drum 30. This relationship is indicated by curve 15.

70 Furthermore, in the figure, there is shown the relationship between (1) the variation in the ratio of the particles B in the developer consisting of the particles A and the particles B deposited on the development sleeve 2 and (2) the variation in the ratio of the particles B in the developer transferred to a sheet of transfer paper via the photoconductor drum 30. That relationship is indicated by curve 16. As can be seen from curves 80 15 and 16, in the image development step, a developer with a mixing ratio of the particles A to the particles B different from the original mixing ratio of the developer deposited on the development sleeve 2 is transferred to the surface of the photoconductor drum 30. Likewise, in the image transfer step, a developer with a mixing ratio of the particles A to the particles B different from the mixing ratio of the developer deposited on the surface of the photoconductor drum 30 is transferred to a sheet of transfer paper and, accordingly, that mixing ratio is different from the mixing ratio of the developer deposited on the surface of the development sleeve 2. As 95 mentioned previously and as also can be seen from Fig. 9, the particles B are consumed less than the particles A. Therefore, the particles B build up in the developer deposited on the development sleeve 2 in the course of multiple copying. In other words, the ratio of the particles B in the developer deposited on the development sleeve 2 increases in the course of multiple copying, decreasing the volume resistivity of the developer with time and degrading the copy quality.

105 Experiment 1

Developer No. 1-2 (refer to Example 1) consisting of 90 parts by weight of the particles A with the average particle size thereof being 15 μm and 10 parts by weight of the particles B with the average particle size thereof being 5 μm was placed in the developer replenishment tank 11 by an amount capable of covering at least the peripheral surface of the development sleeve 2. In this experiment, before the developer was placed 110 in the developer replenishment tank 11, there was no developer either on the development sleeve 2 or in the developer replenishment tank 11.

115 With the start of copying process, the peripheral surface of the development sleeve 2 was uniformly covered with the developer. The quantity of the developer that can cover the peripheral surface of the development sleeve 2 was constant. The developer deposited on the development sleeve 2 consisted of 90 parts by weight of the particles A and 10 parts by weight of the particles B, the mixing ratio of which was exactly the same as that of the developer placed initially in the developer replenishment tank 11.

After image development, the mixing ratio of the particles A to the particles B in the developer deposited on the surface of the photoconductor 30 was measured. The result was that the developer consisted of 93 parts by weight of the particles A and 7 parts by weight of the particles B. Refer to Fig. 9.

In the image transfer step, the developer deposited on the photoconductor 30 was then transferred to a sheet of transfer paper and the mixing ratio of the particles A to the particles B in the developer deposited on the transfer paper was measured. The result was that the developer consisted of 96 parts by weight of the particles A and 4 parts by weight of the particles B. Refer to Fig. 9.

In the case where the developer remaining on the photoconductor drum 30 was recovered and reused, a developer consisting of 96 parts by weight of the particles A and 4 parts by weight of the particles B, the mixing ratio of which was exactly the same as the mixing ratio of the developer transferred to the transfer paper, was supplied to the developer replenishment tank 11, whereby the original mixing ratio of the particles A to the particles B (i.e., 90:10) of the developer deposited on the development sleeve 2 was maintained and a high quality copy was obtained.

It must be noted again that the quantity of the developer that can cover the peripheral surface of the development sleeve 2 was substantially constant.

In the case where the developer remaining on the photoconductor drum 30 was removed after image transfer, without recovering the same, a developer consisting of 93 parts by weight of the particles A and 7 parts by weight of the particles B, the mixing ratio of which was exactly the same as the mixing ratio of the developer transferred to the surface of the photoconductor drum 30, was supplied to the developer replenishment tank 11, whereby the original mixing ratio of the particles A to the particles B (i.e., 90:10) of the developer deposited on the development sleeve 2 was maintained and another high quality copy was also obtained.

Experiment 2

Experiment 1 was repeated except that Developer No. 1-2 was replaced with Developer No. 1-3 consisting of 70 parts by weight of the particles A and 30 parts by weight of the particles B.

The developer deposited on the development sleeve 2 consisted of 70 parts by weight of the particles A and 30 parts by weight of the particles B, the mixing ratio of which was exactly the same as that of the developer placed initially in the developer replenishment tank 11.

After image development, the mixing ratio of the particles A to the particles B in the developer deposited on the surface of the photoconductor 30 was measured. The result was that the developer consisted of 80 parts by weight of the

particles A and 20 parts by weight of the particles B. Refer to Fig. 9.

In the image transfer step, the developer deposited on the photoconductor 30 was then transferred to a sheet of transfer paper and the mixing ratio of the particles A to the particles B in the developer deposited on the transfer paper was measured. The result was that the developer consisted of 90 parts by weight of the particles A and 10 parts by weight of the particles B. Refer to Fig. 9.

In the case where the developer remaining on the photoconductor drum 30 was recovered and reused, a developer consisting of 80 parts by weight of the particles A and 20 parts by weight of the particles B, the mixing ratio of which was exactly the same as the mixing ratio of the developer transferred to the sheet of transfer paper, was supplied to the developer replenishment tank 11, whereby the original mixing ratio of the particles A to the particles B (i.e., 70:30) of the developer deposited on the development sleeve 2 was maintained and another high quality copy was obtained.

In the case where the developer remaining on the photoconductor drum 30 was removed after image transfer, without recovering the same, a developer consisting of 90 parts by weight of the particles A and 10 parts by weight of the particles B, the mixing ratio of which was exactly the same as the mixing ratio of the developer transferred to the surface of the photoconductor drum 30, was supplied to the developer replenishment tank 11, whereby the original mixing ratio of the particles A to the particles B (i.e., 70:30) of the developer deposited on the development sleeve 2 was maintained and another high quality copy was also obtained.

Experiment 3

Experiment 1 was repeated except that Developer No. 1-2 was replaced with Developer No. 4 consisting of 90 parts by weight of the particles A-4 and 10 parts by weight of the particles B-4.

The developer deposited on the development sleeve 2 consisted of 90 parts by weight of the particles A-4 and 10 parts by weight of the particles B-4, the mixing ratio of which was exactly the same as that of the developer placed initially in the developer replenishment tank 11.

After image development, the mixing ratio of the particles A to the particles B in the developer deposited on the surface of the photoconductor 30 was measured. The result was that the developer consisted of 93 parts by weight of the particles A-4 and 7 parts by weight of the particles B-4.

In the image transfer step, the developer deposited on the photoconductor 30 was then transferred to a sheet of transfer paper and the mixing ratio of the particles A-4 to the particles B-4 in the developer deposited on the transfer paper was measured. The result was that the developer

consisted of 96 parts by weight of the particles A-4 and 4 parts by weight of the particles B-4.

In the case where the developer remaining on the photoconductor drum 30 was recovered and reused, a developer consisting of 96 parts by weight of the particles A-4 and 4 parts by weight of the particles B-4, the mixing ratio of which was exactly the same as the mixing ratio of the developer transferred to the sheet of transfer paper, was supplied to the developer replenishment tank 11, whereby the original mixing ratio of the particles A-4 to the particles B-4 (i.e., 90:10) of the developer deposited on the development sleeve 2 was maintained and another high quality copy was obtained.

In the case where the developer remaining on the photoconductor drum 30 was removed after image transfer, without recovering the same, a developer consisting of 93 parts by weight of the particles A-4 and 7 parts by weight of the particles B-4, the mixing ratio of which was exactly the same as the mixing ratio of the developer transferred to the surface of the photoconductor drum 30, was supplied to the developer replenishment tank 11, whereby the original mixing ratio of the particles A-4 to the particles B-4 (i.e. 90:10) of the developer deposited on the development sleeve 2 was maintained and another high quality copy was also obtained.

Multiple copies were then made by repeating the procedure in Experiment 3 and it was observed that the particle size of the particles A-4 gradually increased in the course of the multiple copying, and the particles A-4 with increased particle size were gradually built up in the developer. As a result, the sharpness of the copy image obtained was slightly degraded over time in the course of the multiple copying process.

With the intention of preventing the increase of the particle size of the particles A-4 in the course of multiple copying, the following experiment was conducted, in which the particles A-4 were replaced by particles A-5 whose average particle size was smaller than the particle size of the particles A-4.

Experiment 4

A copy was made under the same conditions as in Experiment 3.

In the case where the developer remaining on the photoconductor drum 30 was recovered and reused, Developer No. 5-1 consisting of 96 parts by weight of the particles A-5 with the average particle size thereof being $12\ \mu\text{m}$ and 4 parts by weight of particles B-5 with the average particle size thereof being $5\ \mu\text{m}$, the mixing ratio of which was exactly the same as the mixing ratio of the developer transferred to the sheet of transfer paper, was supplied to the developer replenishment tank 11, whereby the original mixing ratio of the particles A-4 to the particles B-4 (i.e., 90:10) of the developer deposited on the development sleeve 2 was maintained and high quality copies were continuously obtained in the

course of multiple copying.

In the case where the developer remaining on the photoconductor drum 30 was removed after image transfer, without recovering the same, Developer No. 5-2 consisting of 93 parts by weight of the particles A-5 with the average particle size thereof being $12\ \mu\text{m}$ and 7 parts by weight of the particles B-5, the mixing ratio of which was exactly the same as the mixing ratio of the developer transferred to the surface of the photoconductor drum 30, was supplied to the developer replenishment tank 11, whereby the original mixing ratio of the particles A-4 to the particles B-4 (i.e., 90:10) of the developer deposited on the development sleeve 2 was maintained and high quality copies were also obtained in the course of multiple copying.

In Experiment 4, an increase in the average particle sizes of the particles A-4 and the particles B-4 was not observed and, accordingly, the sharpness of the copy image was maintained.

Furthermore, in Experiment 4 were employed the particles B-5 whose average particle size was the same as that of the particles B-4. However, particles with smaller particle size than that of the particles B-5 can also be used.

In the present invention, as the high volume resistivity particles, magnetic toner is employed. However, non-magnetic toner with the volume resistivity thereof being more than $10^{13}\ \Omega\ \text{cm}$ can also be used. For example, non-magnetic toner comprising 95 to 85 parts by weight of a styrene-acrylate copolymer and 5 to 15 parts by weight of carbon black, with the particle size thereof being in the range of $10\ \mu\text{m}$ to $30\ \mu\text{m}$, when necessary with addition of less than 5 parts by weight of a dye thereto, can be employed.

Claims

1. An electrophotographic process of causing a developer to be attracted, in the form of a brush, to the peripheral surface of a development sleeve with inner magnets, supplying said developer attracted to said development sleeve to a latent electrostatic image formed on a latent electrostatic image bearing member to develop said latent electrostatic image, and transferring said developed image to a sheet of transfer material, wherein said developer comprises a mixture of high volume resistivity particles with the volume resistivity thereof being not less than $10^{13}\ \Omega\ \text{cm}$, and low volume resistivity particles with the volume resistivity thereof being not more than $10^{10}\ \Omega\ \text{cm}$, and the volume resistivity of said developer is changeable, depending upon the intensity of electric field applied thereto, in the range from a low volume resistivity allowing development of said latent electrostatic image on said image bearing member to a high volume resistivity allowing image transfer of said developed image from said latent image bearing member to said sheet of transfer material.

2. An electrophotographic process as claimed in claim 1, wherein the particle size of said high volume resistivity particles is in the range of $5\ \mu\text{m}$

to 30 μm and the average particle size thereof is in the range of 1/5 to 1/2 the average particle size of said low volume resistivity particles.

5 3. An electrophotographic process as claimed
in claim 1, wherein said high volume resistivity
particles are magnetic toner and said low volume
resistivity particles are an electrostatic induction
promoting agent, which serves to make said
10 developer electrically conductive at the time of
development, with the volume resistivity of said
developer being not more than $10^6 \Omega \text{ cm}$ under an
electric field of not less than 10^4 V/cm , and being
not less than $10^{13} \Omega \text{ cm}$ at the time of image
transfer.

15 4. An electrophotographic process as claimed
in claim 2, wherein said high volume resistivity
particles comprise about 70 to about 35 weight
percent of a resinous material, and about 30 to
65 weight percent of a magnetic material.

20 5. An electrophotographic process as claimed
in claim 1, wherein said developer remaining on
said latent electrostatic image bearing member
after image transfer is recovered and reused, and
a developer having the same mixing ratio of said
25 high volume resistivity particles to said low
volume resistivity particles as the mixing ratio of
said two types of particles in said developer
transferred to said sheet of transfer material is
replenished to said development sleeve in the
30 course of multiple copying, whereby the original
mixing ratio of said high volume resistivity
particles to said low volume resistivity particles in
said developer can be maintained.

35 6. An electrophotographic process as claimed
in claim 1, wherein said developer remaining on
said latent electrostatic image bearing member
after image transfer is removed, without being
recovered, and a developer having the same
40 mixing ratio of said high volume resistivity
particles to said low volume resistivity particles as
the mixing ratio of said two types of particles in
said developer deposited on said latent image
bearing member is replenished to said
45 development sleeve in the course of multiple
copying, whereby the original mixing ratio of said
high volume resistivity particles to said low
volume resistivity particles in said developer can
be maintained.

50 7. An electrophotographic process as claimed
in claim 5 and claim 6, wherein the average
particle size of the high resistivity particles in said
developer secondly employed for replenishment is
smaller than the average particle size of said high
55 resistivity particles in said developer first
employed.

60 8. An electrophotographic process as claimed
in claim 5 and claim 6, wherein the average
particle size of the low resistivity particles in said
developer secondly employed for replenishment is
smaller than the average particle size of said high
65 resistivity particles in said developer first
employed.

9. An electrophotographic process
substantially as hereinbefore described, with
reference to the accompanying drawings.