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(71) Applicant: MITA INDUSTRIAL CO., LTD.
2-28, 1-chome, Tamatsukuri Chuo-ku
Osaka 540 (JP)

(72) Inventor: Komata, Hiroshi
1-5-20-404 Tsunematsu
Amagasaki-shi, Hyogo-ken (JP)
Inventor: Tsuji, Nobuyuki
2B Awazu Haitsu, 117-1 Awazu, Kakogawa-cho
Kagogawa-shi, Hyogo-ken (JP)
Inventor: Kimura, Takahiko
201 Yuuki Haimu, 3311 Onda-cho, Midori-ku
Yokohama-shi, Kanagawa-ken (JP)
Inventor: Asada, Hidenori
No 204, 3-5-1 Fujisaka-higashi-machi
Hirakata-shi, Osaka-fu (JP)
Inventor: Yamada, Shigeki
6 Tezukayama 6-chome
Nara-shi, Nara-ken (JP)

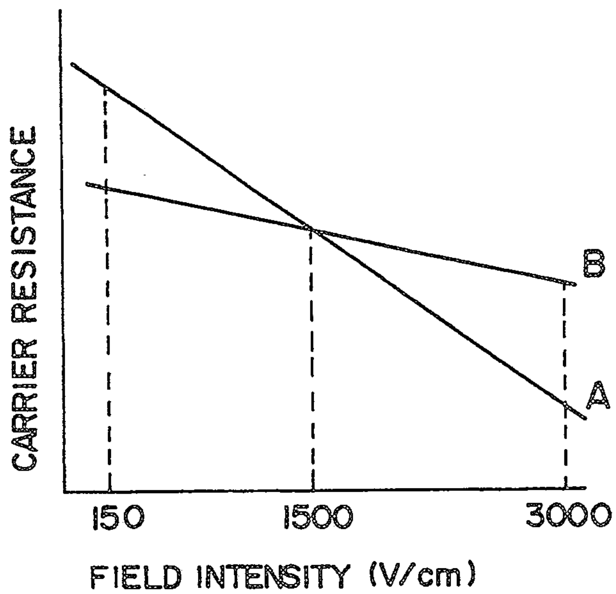
(74) Representative: Williams, Trevor John et al
J.A. KEMP & CO. 14 South Square Gray's Inn
London WC1R 5LX (GB)

(54) **Two-component developer for developing electrostatic images.**

(57) Disclosed is a two-component developer, which comprises, as the carrier, specific sintered ferrite particles obtained by modifying ferrite particles obtained by modifying ferrite customarily used for a carrier, and which can provide a copies image having a high quality, while improving the stirring property and flowability of the carrier. This carrier comprises sintered ferrite particles having an internal pore ratio, based on the area, of 20 to 30% in an amount of 50 to 80% by weight based on the entire carrier, and the developing voltage dependency of the electric resistance of the carrier is reduced and controlled to an appropriate level.

Jouve, 18, rue Saint-Denis, 75001 PARIS

FIG. 1



Background of the Invention

The present invention relates to a two-component developer for use in the electrophotography. More particularly, the present invention relates to a developer, the stirring property of which in a developing apparatus is improved by modifying sintered ferrite particles to be used as the carrier and which is capable of providing a copied image having a high quality.

In the field of the electrophotographic process, a two-component magnetic developer is widely used as the means for developing an electrostatic latent image. In this developing process, the two-component developer composition is supplied onto a developing sleeve having a magnet disposed in the interior thereof to form a magnetic brush compose of this developer composition, and this magnetic brush is brought into sliding contact with a photosensitive plate to form an electroscopic toner image on the photosensitive plate. The electroscopic toner is charged with electricity of a polarity reverse to the polarity of the charge of the electrostatic latent image on the photosensitive plate by the friction with the magnetic carrier, and the electroscopic toner particles on the magnetic brush are caused to adhere to the electrostatic latent image by the Coulomb force to effect of the development of the electrostatic latent image. On the other hand, the magnetic carrier is attracted by the magnet in the sleeve and the applied charge polarity is the same as that of the electrostatic latent image, and therefore, the magnetic carrier is left on the sleeve.

An iron powder carrier has heretofore been widely used as the magnetic carrier, but recently, a sintered ferrite particle carrier is often used instead of the iron powder carrier. The sintered ferrite particle carrier is characterized in that the chemical properties or magnetic characteristics are more stable than those of the iron powder carrier and the particle size and magnetic properties can be easily controlled.

In Japanese Unexamined Patent Publication No. 63-2076, we have proposed a two-component developer for the electrophotography, which comprises a ferrite carrier and an electroscopic fixing toner, wherein the ferrite carrier is composed of ferrite particles in which the relation between the developing voltage and the current density is represented by the Schottky plot, that is, a linear relation is established between the value obtained by raising the field intensity to 1/2-th power and the natural logarithm of the current density.

The Schottky effect referred to in this prior art technique means the effect of further increasing the saturation current by the rise of the developing voltage by emission of electrons, and in this prior art technique, the control of the electroconductivity by the Schottky emission of electrons from a low-electric-resistance ferrite surface layer to a high-electric-resistance ferrite core is utilized.

However, the electric resistance of the conventional magnetic carrier composed of sintered ferrite particles is large on the side of a low electric field and is reduced on the side of a high electric field, and because of this developing voltage dependency, if it is intended to eliminate tailing or scattering of the toner, a brush mark or the like is formed in a solid image area and the image quality is not sufficiently satisfactory.

The sintered ferrite is stirred with the toner in the-apparatus and is them supplied to a developing sleeve, but since the density of the carrier per se is often high and hence, the torque of stirring the developer tends to increase at the step of stirring the carrier with the toner. Moreover, the saturation magnetization per unit of the conventional carrier is low and adhesion of the carrier (carrier dragging) is often caused at the high-speed development.

Summary of the Invention

We found that if sintered ferrite particles having a specific internal pore ratio, a specific electric resistance and a specific developing voltage dependency are used as the magnetic carrier of a two-component developer, the above-mentioned defects of the conventional ferrite carrier are eliminated and the torque of stirring the two-component developer in the apparatus can be drastically reduced. We have now completed the present invention based on this finding.

It is therefore a primary object of the present invention to provide a two-component developer capable of forming images having a good quality without such troubles as formation of brush marks, carrier dragging, tailing, fogging and scattering of the toner.

Another object of the present invention is to provide a two-component developer, in which the torque of stirring the toner and carrier in the apparatus can be drastically reduced.

Still another object of the present invention is to provide a developer, which is suitable for high-speed development.

In accordance with the present invention, there is provided a two-component developer comprising a magnetic carrier and an electroscopic toner, said magnetic carrier comprising sintered ferrite particles having an internal pore ration, based on the area, of 20 to 30% in an amount of 50 to 80% by weight based on the total particles, having an electric resistance of 1×10^8 to 1×10^{10} Ω-cm under a field intensity of 1500 V/cm, and having a developing voltage dependency (R_{150}/R_{1500}), defined as the ratio of the electric resistance (R_{150}) under a field intensity of 150 V/cm to said electric resistance (R_{1500}) under a field intensity of 1500 V/cm, of from 5 to 20.

Preferably, this carrier has a volume median particles diameter of 30 to 50 μm, an apparent density of 1.8 to 2.5 g/cc, such a particle size distribution that the content of particles having a size smaller than 400 mesh is 20 to 40% by weight, a flowability of 20 to 30 sec/50 g (JIS Z-2502), a saturation magnetization of 50 to 60 emu/g and a specific surface area of 0.02 to 0.20 m^2/g.

In accordance with another aspect of the present invention, there is provided a two-component developer for developing an electrostatic image, comprising a magnetic carrier and an electroscopic toner, said magnetic carrier comprising sintered ferrite particles having an internal pore ratio, based on the area, of 20 to 30% in an amount of 50 to 80% by weight based on the total particles, having an electric resistance of 1×10^7 to 1×10^{11} Ω-cm under a field intensity of 2500 V/cm, and having a developing voltage dependency (R_{2500}/R_{5000}), defined as the ratio of the electric resistance (R_{5000}) under a field intensity of 5000 V/cm to said electric resistance (R_{2500}) under a field intensity of 2500 V/cm, of from 1.5 to 20, a volume median particle diameter of 70 to 110 μm, an apparent density of 2.0 to 3.0 g/cc and a saturation magnetization of 40 to 60 emu/g.

Preferably, this carrier has a flowability of 20 to 30 sec/50 g (JIS Z-2502), or this carrier has a specific surface area of 0.02 to 0.20 m^2/g.

Brief Description of the Drawings

Fig. 1 and 2 are diagrams illustrating relations between the resistance of the carrier and the field intensity.

Fig. 3 is a diagram illustrating the internal particles structure of the carrier of the present invention, observed by an electron microscope.

Detailed Description of the Preferred Embodiments

The present invention provides a two-component developer comprising a magnetic carrier composed of a specific amount of ferrite particles having an internal pore ratio, based on the area, of 20 to 30%, especially 25 to 30%. Namely, it is important that a carrier comprising ferrite particles having an internal pore ratio within the above-mentioned range in an amount of 50 to 80% by weight based on the total particles should be used. The internal pore ratio based on the area, referred to herein, is a value determined by cutting the carrier particle through the center thereof by a microtome and making a calculation from a microscope photo of the section according to the following formula:

$$\text{Internal pore ratio (Pr)} = \frac{\text{sectional area of pores}}{\text{entire sectional area of particle}} \times 100\ (\%) \qquad (1)$$

The present invention is based on the finding that the content of particles having a specific internal pore ratio based on the area in sintered ferrite particle has a serious influence on the developing voltage dependency of the electric resistance and this developing voltage dependency makes great contributions to improvement of the image quality.

The developing voltage dependency referred to herein means the value defined by the following formula:

$$\text{Developing voltage dependency (De)} = \frac{R_{150}}{R_{1500}} \qquad (2)$$

wherein R_{1500} represents the electric resistance value (Ω-cm) of the magnetic carrier as measured under a field intensity of 1500 V/cm, and R_{150} represents the electric resistance (Ω-cm) of the magnetic carrier as measured under a field intensity of 150 V/cm.

In the instant specification, the developing voltage dependency has the following significance. The reason why the electric resistance of the denominator of the formula (2) is determined under an electric field of 1500 V/cm is that the field intensity attained when the bias voltage is applied to the developing sleeve is substantially of the same order as the above field intensity. Furthermore, the reason why the electric resistance of the numerator of the formula (2) is determined under a field intensity of 150 V/cm is that the field intensity attained when the toner and carrier are charged is lower than 1/10 of the field intensity attained when the bias voltage is applied to the developing sleeve and hence, the electric resistance of this case is brought close to the above electric resistance. Namely, in the state where the field intensity is low, the surface resistance of the carrier particles makes a larger contribution to the electric resistance of the magnetic carrier, and in the state where the electric field is high, the internal resistance of the carrier particles makes a larger contribution to the electric resistance of the magnetic carrier. Accordingly, in magnetic carrier particles, in general, the surface resistance is mainly a resistance value under a low field intensity and the internal resistance is mainly a resistance value under a high field intensity. Therefore, the developing voltage dependency can be regarded as expressing the ratio between the surface resistance and the internal resistance or the gradient of the change of the resistance in the region of from a low field intensity to a high field intensity.

As pointed out hereinbefore, the internal pore ratio, based on area, of the ferrite particles has serious influences on the developing voltage dependency of the electric resistance, and with increase of the internal pore ratio in the sintered ferrite particles, the denominator R_{1500} of the formula (2) increase while the numerator R_{150} of the formula (2) decreases. In short, the surface resistance of sintered ferrite is brought close to the internal resistance. In this point, the sintered ferrite particles of the present invention are prominently distinguishable over the conventional sintered ferrite particles in which the developing voltage dependency of the electric resistance is extremely large.

Fig. 1 of the accompanying drawings is a graph illustrating the dependency of the electric resistance of the magnetic carrier on the developing voltage. Curve A shows the dependency of the conventional sintered ferrite carrier (content of particles having Pr lower than 3% is 70% and De is 25), and curve B shows the dependency of the sintered ferrite carrier (content of particles having Pr of 20 to 30% is 70% and De is 10) used in the present invention.

In the present invention, if the content of particles having an internal pore ratio (Pr), based on the area, of 20% to 30% is lower than 50%, the torque of stirring the magnetic carrier with the toner increases too much at the development. If the content of particles having an internal pore ratio lower 3% increases, it becomes difficult to adjust the developing voltage dependency (De) within the range specified in the present invention, however controlled the ferrite substrate may be, and therefore, formation of brush marks or carrier dragging is often caused. If the content of particles having an internal pore ratio (Pr) higher than 30% increases, the particles strength of the magnetic carrier is reduced and the magnetic carrier is readily destroyed under magnetic brush development conditions, and the life of the developer becomes short.

In the present invention, the electric resistance R_{1500} under a field intensity of 1500 V/cm is 1×10^6 to 1×10^{10} Ω-cm, especially 1×10^7 to 1×10^9 Ω-cm, while the internal pore ratio (Pr) is within the above-mentioned range, and the developing voltage dependency (De) is adjusted to 5 or 20. If the electric resistance R_{1500} under a field intensity of 1500 V/cm is within the above-mentioned range, carrier dragging and background fogging can be effectively prevented in the state where the bias voltage is applied to the developing sleeve, and if the developing voltage dependency is within the above-mentioned range, scattering of the toner and formation of brush marks can be prevented and an image having an excellent gradation can be obtained. If the developing voltage dependency (De) is smaller than 5, scattering of the toner or tailing is caused by insufficient charging of the toner, and if the developing voltage dependency is larger than 20, the change of the carrier resistance in the developing bias voltage acting between the electrostatic latent image and the bias voltage applied to the developing sleeve becomes too large and by leakage of the charge on the surface of the photosensitive material, brush marks are formed.

In the instant specification, brush marks mean white fine streaks formed in a solid image, and the carrier dragging means the development of an electrostatic latent image not only by the toner but also by the carrier. Namely, adhesion of the carrier to the toner image is meant. The tailing means the adhesion of the toner to the surrounding portion of the normal image and this phenomenon resembles the fogging in that the toner adheres to a portion other than the normal image.

Preferably, the volume median particle diameter and apparent density of the carrier are within the above-mentioned ranges. This volume median particle diameter is relatively small as the particle size of the magnetic carrier and this apparent density is relatively low as the apparent density of the magnetic carrier. If the volume median particle diameter and apparent density of the carrier are within the above-mentioned ranges, even if the toner concentration is changed, the change of the ratio of the toner particles present among the carrier particles is small and hence, the allowable range of the toner concentration for forming an image having a good quality is broadened and destroy of the carrier particles by mutual friction can be prevented.

In order to further improve the image quality, it is preferred that the magnetic carrier should have the above-mentioned particle size distribution. Namely, if the content of fine particles having a particle size smaller than 400 mesh is adjusted to 20 to 40% by weight, the magnetic brushes on the developing sleeve can be softened.

If the content of particles having the above-mentioned particle size is lower than 20% by weight, the brushes become rigid and the image quality is often degraded. The influences of the particle size distribution is especially serious in ferrite particles having a high pore ratio.

Preferably, the carrier has a saturation magnetization of 50 to 60 emu/g. If the saturation magnetization exceeds this range, the brushes are rigid and the image quality is often degraded. If the saturation magnetization is below the above-mentioned range, carrier dragging is readily caused. In contrast, if the saturation magnetization is within the above-mentioned range, the image quality can be improved while preventing scattering of the carrier.

For the carrier of the developer to be used mainly for high-speed development, it is preferred that the developing voltage dependency be controlled within a certain range.

The developing voltage dependency is represented by the following formula:

$$\text{Developing voltage dependency (De)} = \frac{R_{2500}}{R_{5000}} \quad (3)$$

wherein R_{2500} represents the electric resistance value (Ω-cm) of the magnetic carrier as measured under a field intensity of 2500 V/cm, and R_{5000} represents the electric resistance value (Ω-cm) of the magnetic carrier as measured under a field intensity of 5000 V/cm.

The developing voltage dependency has the following significance. The reason why the electric resistance of the denominator of the formula (3) is determined under a field intensity of 5000 V/cm is that the minimum value of the intensity of the developing voltage applied to the magnetic brush at the development, that is, the charge intensity acting between the surface voltage on the photosensitive material and the bias voltage applied to the developing sleeve, is almost equal to the above-mentioned intensity value. The reason why the electric resistance of the numerator of the formula (3) is determined under a field intensity of 2500 V/cm is that the field intensity by the bias voltage applied to the developing sleeve is this value and has influences on adhesion of the carrier and background fogging.

If the internal pore ratio based on the area of the ferrite particles is within the above-mentioned range, the internal pore ratio has important influences on the developing voltage dependency, and as the internal pore ratio increases in the sintered ferrite particles, the R_{5000} value of the denominator of the formula (3) increases while the R_{2500} value of the numerator decreases.

Fig. 2 of the accompanying drawings illustrates the dependency of the electric resistance of the magnetic carrier on the developing voltage. Curve A shows the dependency of the conventional sintered ferrite carrier (the content of particles having a pore ratio Pr lower than 3% is 75% by weight and De is 30), and curve B shows the dependency of the sintered ferrite carrier of the present invention (the content of particle having a pore ratio of 20 to 30% is 70% by weight and De is 10).

If the internal pore ratio (Pr) based on the area is within the above-mentioned range, the developing voltage dependency (De) of the carrier can be adjusted within the range of from 1.5 to 20, and the change or gradient of the electric resistance to the developing voltage can be made gentle in a region of from a low voltage to a high voltage.

From the viewpoint of the image quality, it is important that the R_{2500} value of the carrier should be selected within the range of from 1×10^7 to 1×10^{11} Ω-cm, especially 1×10^8 to 5×10^{10}. It also is important that the apparent density of the carrier should be 2.0 to 3.0 g/cc, especially 2.2 to 2.8 g/cc, and the volume median particle diameter of the carrier particles should be 70 to 110 μm, especially 80 to 100 μm. If ferrite particles satisfying the forgoing requirements are used for the two-component developer, the saturation magnetization of one carrier particle is maintained stably at a high level, and at the high-speed development, the adhesion of the carrier can be prevented and an image having an excellent quality can be obtained at a high speed.

Furthermore, it is important that the saturation magnetization should be 40 to 60 emu/g, especially 45 to 55 emu/g. If the saturation magnetization of the ferrite particles is within this range, the developer brush formed on the surface of the developing sleeve can be kept soft, and the image quality can be improved. Moreover, carrier dragging can be prevented and the distance D-S between the photosensitive drum and the developing sleeve can be diminished.

Preferably, the carrier for ordinary development and the carrier for high-speed development have a flowability of 20 to 30 sec/50 g, especially 20 to 28 sec/50 g. This flowability is expressed by the time required for a certain weight (50 g) of particles to pass through the orifice. A larger value indicates a poor flowability and a smaller value indicates a better flowability. The flowability depends on the particle size and particle shape, but if the above-mentioned particle size conditions are satisfied, a carrier having a flowability within the above-mentioned range is composed of particles having a substantially uniform spherical shape and an excellent pulverization resistance. Also from this viewpoint, particles having a high pore ratio are preferably use.

The magnetic carrier has a specific surface area of 0.02 to 0.20 m²/g as determined by the BET method.

This characteristic value depends on the surface state of the particles if the particle size conditions are the same. If the specific surface area is adjusted within this range, the pulverization resistance is preferably increased.

The present invention will now be described in detail.

Magnetic Carrier

Sintered ferrite particles used in the present invention have a known ferrite composition. As the magnetic pigment, there can be mentioned zinc iron oxide ($ZnFe_2O_4$), yttrium iron oxide ($Y_3Fe_5O_{12}$), cadmium iron oxide ($Cd_3Fe_5O_{12}$), gadolinium iron oxide ($Ge_3Fe_5O_7$), copper iron oxide ($CuFe_2O_4$), lead iron oxide ($PbFe_{12}O_{19}$), neodium iron oxide ($NbFeO_3$), barium iron oxide ($BaFe_{12}O_{19}$), magnesium iron oxide ($MgFe_2O_4$), manganese iron oxide ($MnFe_2O_4$) and lanthanum iron oxide ($LaFeO_3$). These magnetic pigments can be used singly or in the form of a mixture of two or more of them. Soft ferrites comprising at least one metal component, especially at least two metal components, selected from the group consisting of Cu, Zn, Mg and Ni, for example, a copper/zinc/magnesium ferrite, are preferable used, and a ferrite comprising 35 to 70 mole% of Fe_2O_3, 5 to 15 mole% of CuO, 5 to 35 mole% of ZnO, and 0 to 40 mole% of MgO and other metal oxides is especially preferably used.

The ferrite composition is formed into sintered particles so that the above-mentioned internal pore ratio based on the area and the above-mentioned developing voltage dependency of the electric resistance are attained. In general, as the primary particle size of oxide particles constituting the ferrite increases, the internal pore ratio becomes high, and as the primary particle size decreases, the internal pore ratio tends to drop. At the preparation of ferrite particles by sintering, as the sintering degree is high, the internal pore ratio tends to drop. For example, the higher is the sintering temperature, the lower is the internal pore ratio, and the longer is the sintering time, the lower is the internal pore ratio. Of course, as the particle size of the starting ferrite or intermediate is fine, sintering is advanced under milder conditions than in case of particles having a large size. Accordingly, these factors should be carefully combined.

The internal pore-containing sintered ferrite can be prepared, for example, according to a process in which a starting metal oxide or intermediate having a primary particle size of 0.1 to 2.0 μm is shaped into a predetermined particulate form and sintered at a temperature of 900 to 1500°C for 5 to 50 hours, though the preparation process is not limited to this process.

It is necessary that the electric resistance of the carrier under a field intensity of 1500 V/cm should be arranged within the above-mentioned range of 1×10^6 to 1×10^{10} Ω-cm by appropriately combining the material and the degree of formation of pores. In order to obtain an electric resistance within this range, it is indispensable that particles having a pore ratio of at least 3% should be contained in an amount of at least 50% by weight.

Fig. 3 of the accompanying drawings is a sketch of a microscope photo (800 magnifications) showing the internal structure of the sintered ferrite particle used in the present invention.

In the present invention, it is preferred that the requirements of the volume median particle diameter of 30 to 50 μm and the apparent density of 1.8 to 2.5 g/cc be satisfied as well as the above-mentioned structural requirements.

The volume median particle diameter of the carrier can be adjusted by appropriately selecting the starting ferrite material, the primary particle size and the particle size of the intermediate or according to the sintering conditions. Furthermore, the volume median particle diameter of the obtained ferrite particle can be adjusted within the above-mentioned range according to the known sieving method. The apparent density can be arranged within the above-mentioned range according to methods similar to those mentioned above with respect to the particle size.

As pointed out hereinbefore, it is preferred that the content of particles having a small particle size, that is, a particle size smaller than 400 mesh, be 20 to 40% by weight based on the entire carrier. If this requirement is satisfied as well as the above-mentioned requirements of the particle size and the apparent density, the allowable range of the toner concentration is broadened and the image quality is further improved. Furthermore, it is preferred that the saturation magnetization be adjusted to 50 to 60 emu/g. The adjustment of the saturation magnetization is accomplished by appropriately combining the ferrite materials. The so-prepared carrier is advantageous in that scattering of the carrier to the photosensitive material is prevented, and the brush becomes soft and an image having a rich gradation is obtained.

In the carrier to be used mainly for high-speed development, it is necessary that the electric resistance under a field intensity of 2500 V/cm should be 1×10^7 to 1×10^{11} Ω-cm, especially 1×10^8 to 5×10^{10} Ω-cm. If the electric resistance is below the above range, formation of brush marks is not sufficiently prevented at the development. If the electric resistance exceeds the above range, the image density is reduced, background fogging becomes conspicuous and the consumption of the toner increases. The volume median particle diameter is 70 to 110 µm, especially 80 to 100 µm. If the volume median particle diameter is below the above range, not only the apparent density but also the saturation magnetization is lowered at the development, and the adhesion of the carrier is readily caused at the high-speed development. If the volume medial particle diameter exceeds the above-mentioned range, the magnetic brush formed on the surface of the developing sleeve becomes rigid and therefore, the image quality is degraded. Furthermore, the apparent density is adjusted to 2.0 to 3.0 g/cc, especially 2.2 to 2.8 g/cc, while adjusting the internal pore ratio and the volume median particle diameter within the above-mentioned ranges. If the apparent density exceeds the above-mentioned range, stirring load at the development increases, and the saturation magnetization decreases and the adhesion of the carrier cannot be prevented at the high-speed development.

The saturation magnetization of the carrier is adjusted to 40 to 60 emu/g, especially 45 to 55 emu/g. The saturation magnetization can be controlled within the above-mentioned range by changing the ferrite composition. If the saturation magnetization is below the above-mentioned range, carrier dragging is caused at the development, and if the saturation magnetization exceeds the above-mentioned range, the magnetic brush formed on the surface of the developing sleeve becomes rigid and the image quality is degraded.

Toner

Any of colored toners having electroscopic and fixing properties can be used as the toner together with the carrier of the present invention. Namely, a granular composition having a particle size of 5 to 30 µm, which is formed by dispersing a coloring pigment, a charge-controlling agent and the like into a binder resin, is used. As the binder resin, there can be used a thermoplastic resin, an uncured thermosetting resin and a precondensate thereof. As specific examples, there can be mentioned, in order of the importance, a vinyl aromatic resin such as polystyrene, an acrylic resin, polyvinyl acetal, a polyester, an epoxy resin, a phenolic resin, a petroleum resin and an olefin resin. As the pigment, there can be used, for example, at least one member selected from the group consisting of carbon black, cadmium yellow, molybdenum orange, Pyrazolone Red, Fast Violet B and Phthalocyanine Blue. As the charge-controlling agent, there can be used oil-soluble dyes such as Nigrosine Base (CI 50415) and Oil Black (CI 26150), and a metal salt of naphthenic acid, a metal soap of a fatty acid, a metal-containing azo dye and a metal salt of an alkylsalicylic acid according to need.

The electroscopic toner particles used in the present invention have such particle characteristics that the median particle diameter is 10 to 35 µm and the content of particles having a size smaller than 5 µm is substantially zero.

Two-Component Developer

The two-component developer is formed by mixing at least 85% by weight, especially 90 to 95% by weight, of the magnetic carrier, with up to 15% by weight, especially 5 to 10% by weight, of the toner. The developer having this composition is mixed and stirred, supplied onto the developing sleeve having a magnet disposed in the interior thereof and brought into sliding contact with the surface of the photosensitive material having an electrostatic image to form a toner image, and the toner image is transferred onto a transfer sheet and is contacted with a heating roller to obtain a copy having a fixed toner image.

According to the present invention, by using sintered ferrite particles having a specific internal pore ratio based on the area, a specific electric resistance and a specific developing voltage dependency as the magnetic carrier of a two-component developer, the gradation of the formed toner image is improved and occurrence of the troubles such as scattering of the toner and carrier dragging can be prevented. Furthermore, the durability of the carrier is satisfactory. Moreover, by adjusting the volume median particle diameter, saturation magnetization and apparent density within specific ranges, a carrier suitable for high-speed development can be provided.

Examples

The present invention will now be described in detail with reference to the following examples.

Example 1

Ferrite carrier particles having properties shown in Table 1 were mixed with an electroscopic toner obtained by surface-treating 100 parts by weight of toner particles having a median diameter of 13 µm, which were prepared according to customary procedures from a basic composition comprising 100 parts by weight of a styrene/acrylic polymer, 10 parts by weight of carbon black, 1.0 part by weight of a metal-containing azo dye and 1.5 parts by weight of low-molecular-weight polypropylene, with 0.3 part by weight of hydrophobic silica and 0.15 part by weight of alumina to form a two-component developer having a toner concentration of 9%. By using this two-component developer, the printing test for obtaining 50,000 copies was carried out in a remodelled machine of DC-4055 (supplied by Mita Kogyo) under conditions of developing voltage difference of 570 B, bias voltage of 250V and developing speed of 40 sheets per minute.

The obtained copies were evaluated according to the following methods.

(1) Image Density

Samples showing an image density of at least 1.3 as measured by a reflection densitometer were indicated by mark "O" and samples having a lower image density were indicated by mark "X".

(2) Background Fogging

Samples in which the density of the non-copied area was lower than 0.005 as measured by a reflection densitometer were indicated by mark "O" and samples having a higher density in the non-copied area were indicated by mark "X".

(3) Brush Marks

A solid image having an area of 2 cm^2 was copied, and longitudinal streaks formed on the copied image were visually observed.

(4) Carrier Dragging

A solid image having an area of 2 cm^2 was copied, and a white blank portion formed on the top end part of the copied image by adhesion of the carrier was visually checked.

(5) Tailing

A solid image having an area of 2 cm^2 was copied, and bleeding formed in the lower end side portion of the copied image was visually checked.

(6) Gradation

A gray scale image (an original having an image density gradually increasing from the upstream side toward the downstream side) was copied, and the image density of the obtained copy was measured and the reproduction state was examined.

(7) Stirring Property

After the toner concentration had been reduced, the toner was supplied so that a predetermined toner concentration was attained. Then, the developer was stirred for a predetermined time, and the charge quantity of the toner was measured and the state of scattering of the toner was checked.

The obtained results are shown in Table 1.

In each of the measurement items (3) through (7), mark "O" indicates no practical problem, mark "Δ" indicates an allowable level though somewhat insufficient, and mark "X" indicates a practical problem.

From the results shown in Table 1, it is seen that carriers of runs 1 through 4 were excellent in all of the test items, especially in the gradation. In the carrier of run 5, the content of particles having a pore ratio lower than 3% was 43%, and the developing voltage dependency was high and the flowability was low. The carrier of the run 6 had a high electric resistance under a field intensity of 1500 V/cm, and the developing dependency was low. In the carrier of run 7, the content of particles having a pore ratio of 20 to 30% was too high, and the developing voltage dependency was reduced too much. In the carrier of run 8, the content of particles having a pore ratio lower than 3% was too low, and the developing voltage dependency is too high.

Table 1

	Run No.							
	1	2	3	4	5	6	7	8
content (%) of ferrite particles having internal pore ratio lower than 20%	5	5	10	10	20	0	5	45
content (%) of ferrite particles having internal pore ratio of 20 to 30 %	70	75	55	65	40	75	90	30
content (%) of ferrite particles having internal pore ratio higher than 30%	20	10	30	15	10	20	0	10
electric resistance (at 1500V/cm)	8.5×10^7	1.1×10^7	1.8×10^9	8.8×10^7	2.3×10^7	1.4×10^{10}	1.2×10^8	2.5×10^7
developing voltage dependency (R_{150}/R_{1500})	10.8	19.1	6.7	19.9	21.7	2.9	4.4	20.5
median particle size (µm)	45	48	40	47	44	46	41	45
apparent density (g/cc)	2.3	2.0	2.4	2.1	2.1	2.3	2.4	2.6
specific surface area (m^2/g)	0.12	0.15	0.18	0.13	0.16	0.18	0.14	0.14
flowability (sec/50g)	25	24	29	28	35	25	27	23
content (%) of particles having size smaller than 400 mesh	33	31	38	28	43	31	29	31
saturation magnetization (emu/g)	52	54	55	52	54	50	55	55

Table 1 (Cont'd)

	Run No.							
	1	2	3	4	5	6	7	8
image density	○	○	○	○	○	○	○	○
backgroud fogging	○	○	○	○	○	×	○	○
brush mark	○	△	○	△	×	○	○	×
carrier dragging	○	△	○	○	△	△	○	○
tailing	○	○	○	○	○	○	×	○
gradation	○	○	○	○	△	×	×	△
forced supply test (stirring property)	○	○	○	△	×	△	△	×

Note

○: no practical problem

△ : allowable though somewhat insufficient

× : practical problem

Example 2

A two-component developer having a toner concentration of 9% was prepared by using ferrite carriers having properties shown in Table 2 and the same toner composition as used in Example 1, and the copying test for obtaining 50,000 prints was carried out by using this developer in a remodelled machine of DC-4555 (supplied by Mita Industrial Co., Ltd.) under conditions of a developing voltage difference of 500 V, a bias voltage of 250 V and a developing speed of 45 sheets per minute. The obtained results are shown in Table 2.

From the results shown in Table 2, it is seen that carriers of runs 1 through 4 were excellent in all of the test items, especially in the gradation. In the carrier of run 5, the content of particles having a pore ratio of 20 to 30% was high and the developing voltage dependency was too low. In the carrier of run 6, the developing voltage was too high because the content of particles having a pore ratio lower than 3% was high. In the carrier of run 7, the saturation magnetization was too low. In the carrier of run 8, the electric resistance under a field intensity of 2500 V/cm was too high.

Table 2

	Run No.							
	1	2	3	4	5	6	7	8
content (%) of ferrite particles having internal pore ratio lower than 20%	35	20	20	10	5	45	15	10
content (%) of ferrite particles having internal pore ratio of 20 to 30 %	55	70	75	65	90	40	75	60
content (%) of ferrite particles having internal pore ratio higher than 30%	10	10	5	25	5	15	10	30
electric resistance (at 2500V/cm)	1.5×10^7	6.0×10^8	2.5×10^9	6.5×10^9	4.2×10^9	1.2×10^7	3.5×10^8	2.1×10^{11}
developing voltage dependency (R_{2500}/R_{5000})	18.1	8.6	1.9	3.5	1.5	22.2	7.7	2.2
median particle size (μm)	86	103	95	100	92	96	94	100
apparent density (g/cc)	2.5	2.7	2.6	2.5	2.5	2.6	2.3	2.4
specific surface area (m^2/g)	0.15	0.14	0.16	0.15	0.15	0.15	0.14	0.15
flowability (sec/50g)	26	24	25	25	25	24	23	25
saturation magnetization (emu/g)	48	52	50	56	52	55	38	50

Table 2 (Cont'd)

	Run No.							
	1	2	3	4	5	6	7	8
image density	○	○	○	○	○	○	○	X
background fogging	○	○	○	○	○	○	○	○
brush mark	○	○	○	○	○	X	○	○
carrier dragging	△	○	○	○	○	X	X	○
gradation	○	○	△	○	X	△	○	△
forced supply test (stirring property)	○	○	○	○	○	X	△	△

Claims

1. A two-component developer for developing an electrostatic image, comprising a magnetic carrier and an electroscopic toner, said magnetic carrier comprising sintered ferrite particles having an internal pore ratio, based on the area, of 20 to 30% in an amount of 50 to 80% by weight based on the total particles, having an electric resistance of 1×10^6 to 1×10^{10} Ω-cm under a field intensity of 1500 V/cm, and having a developing voltage dependency (R_{150}/R_{1500}), defined as the ratio of the electric resistance (R_{150}) under a field intensity of 150 V/cm to said electric resistance (R_{1500}) under a field intensity of 1500 V/cm, of from 5 to 20.

2. A two-component developer according to claim 1, wherein the volume median particle diameter of the carrier is 30 to 50 μm, the apparent density of the carrier is 1.8 to 2.5 g/cc, the particle size distribution of the carrier is such that the content of particles having a particle size smaller than 400 mesh is 20 to 40% by weight, and the saturation magnetization of the carrier is 50 to 60 emu/g.

3. A two-component developer according to claim 1, wherein the flowability (JIS Z-2502) of the carrier is 20 to 30 sec/50 g.

4. A two-component developer according to claim 1, wherein the specific surface area of the carrier is 0.02 to 0.20 m^2/g (BET method).

5. A two-component developer for developing an electrostatic image, comprising a magnetic carrier and an electroscopic toner, said magnetic carrier comprising sintered ferrite particles having an internal pore ratio, based on the area, of 20 to 30% in an amount of 50 to 80% by weight based on the total particles, having an electric resistance of 1×10^7 to 1×10^{11} Ω-cm under a field intensity of 2500 V/cm, and having a developing voltage dependency (R_{2500}/R_{5000}), defined as the ratio of the electric resistance (R_{5000}) under a field intensity of 5000 V/cm to said electric resistance (R_{2500}) under field intensity of 2500 v/cm, of from 1.5 to 20, a volume median particle diameter of 70 to 110 um, an apparent density of 2.0 to 3.0 g/cc and a saturation magnetization of 40 to 60 emu/g.

6. A two-component developer according to claim 5, wherein the flowability (JIS Z-2502) of the carrier is 20 to 30 sec/50 g.

7. A two-component developer according to claim 5, wherein the specific surface area of the carrier is 0.02 to 0.20 m^2/g (BET method).

FIG. 1

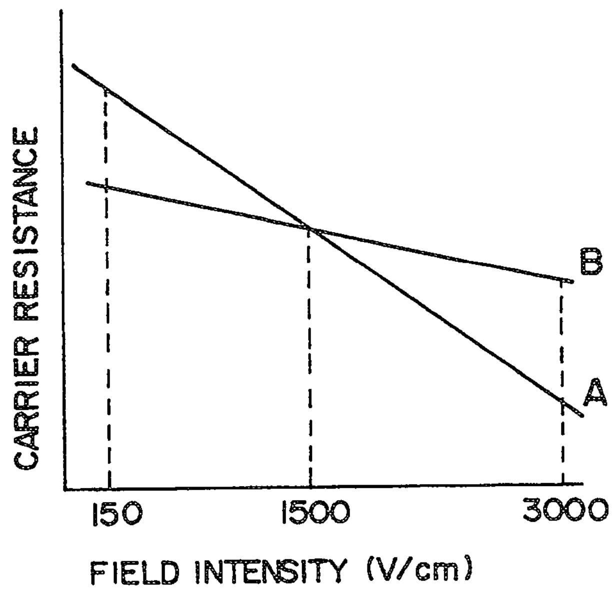

CARRIER RESISTANCE
B
A
150
1500
3000
FIELD INTENSITY (V/cm)

FIG. 2

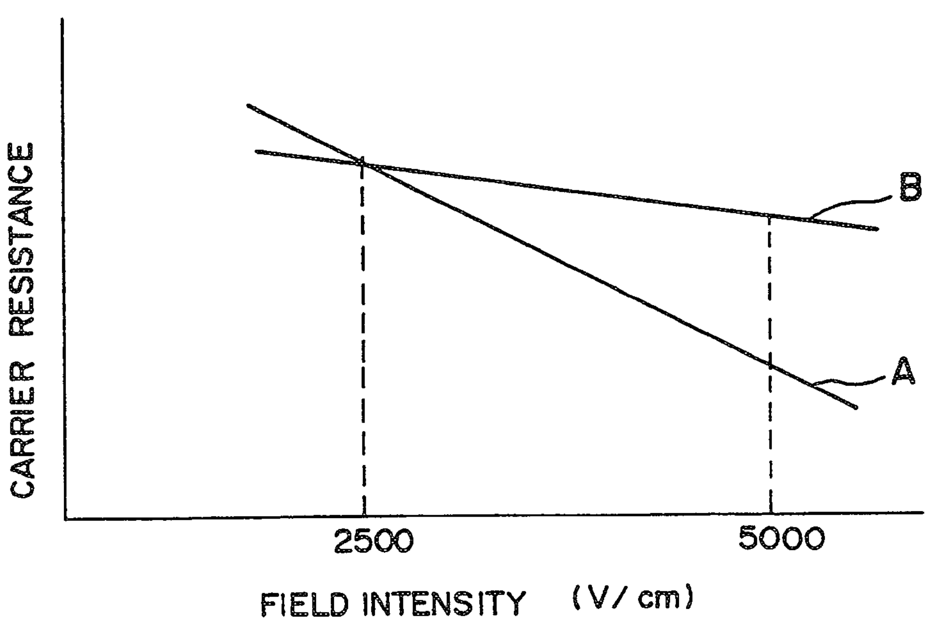
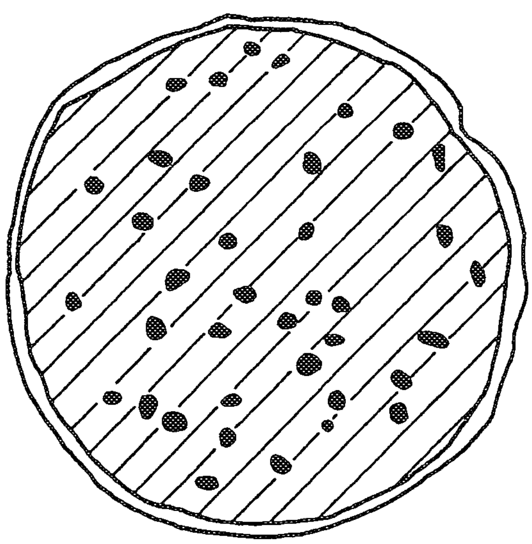

CARRIER RESISTANCE
B
A
2500
5000
FIELD INTENSITY (V/ cm)

FIG. 3



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EUROPEAN SEARCH REPORT

Application Number

EP 91 30 2558

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	WO-A-8601314 (HALOMET, INC.) * claims 1, 2, 4-7, 9 * ---	1-3, 5, 6	G03G9/107
A	US-A-3996392 (BERG ET AL.) * abstract * * column 2, lines 18 - 65 * ---	4, 7	
A	US-A-4614698 (MIYAKAWA ET AL.) * abstract * ---	1-7	
A	PATENT ABSTRACTS OF JAPAN vol. 9, no. 105 (P-354)(1828) 09 May 1985, & JP-A-59 228664 (TDK K.K) 22 December 1984, * the whole document * -----	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G03G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	25 JUNE 1991	VOGT C.

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