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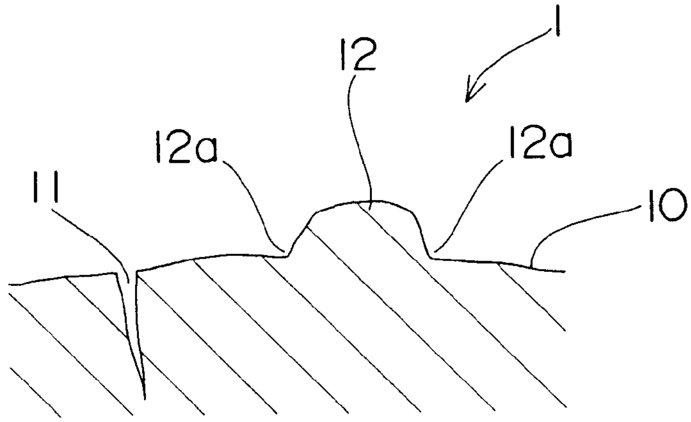
(54) **Electrophotographic carrier**

(57) The electrophotographic carrier of the present invention comprises magnetic particles having such a specific surface state that the adhesion rate of a resin due to a method for forcibly adhering resin is within the range from 0.01 to 0.50%, or magnetic particles wherein at least concave parts and projection peripheral parts of the surface are coated with a resin, thereby certainly preventing the occurrence of spent toner.

Fig. 7



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Description

BACKGROUND OF THE INVENTION

The present invention relates to an electrophotographic carrier.

In image forming apparatus utilizing electrophotography, such as electrostatic copying machines, laser printers, plain paper facsimiles, a two-component developer comprising a toner for developing an electrostatic latent image formed on the surface of a photoconductor and a carrier of a magnetic material is normally used. The carrier circulates in a developing apparatus of the image forming apparatus in the state where the toner is adsorbed by an electrostatic attraction force. As the carrier, magnetic particles such as iron powder and ferrite particles have hitherto been used.

In an image forming apparatus using a two-component developer, the toner or pulverized material thereof adheres to the surface of the carrier when the developer is repeatedly stirred in the developing apparatus, that is, so-called spent toner occurs. Therefore, the charged amount of the carrier is reduced, thereby causing so-called fog wherein the toner adheres to a blank area of the image, toner scattering and the like.

In order to prevent the occurrence of spent toner, the surface of the magnetic particles is coated with a thermosetting or thermoplastic resin.

This coating type carrier has not only the effect of preventing the occurrence of spent toner as described above, but also high electric resistance. Therefore, the carrier is also superior in charge imparting effect for charging the toner and is frequently used.

However, the coating type carrier has high electric resistance as described above and, therefore, the image density of the formed image is liable to be reduced.

The coating type carrier has a problem that the coating of resin comes off from the surface of the magnetic particle by receiving an external force when it is repeatedly circulated in the developing apparatus, thereby lowering the charge imparting effect, or lowering the image quality of the formed image because the resin coming off from the magnetic particles is included in the toner.

Japanese Patent Unexamined Publication No. 61-158339 discloses a carrier wherein a resin is embedded in a concave part of the surface of the magnetic particles, where the toner or pulverized material thereof is most liable to adhere, that is, spent toner is most liable to occur.

Such a carrier is obtained by mixing with stirring the magnetic particles with resin powder having a particle size smaller than that of the magnetic particles to embed the resin powder into the concave part of the magnetic particles. The resin powder embedded into the concave part is melted by heating the magnetic particles and integrated with the magnetic particles. When the resin particles have an electrostatic adhesion force, these heating and melting steps may be omitted.

Since the above carrier is obtained by embedding the resin into the concave part where spent toner is most liable to occur, the occurrence of spent toner is inhibited to some extent. Furthermore, the magnetic particles are exposed except for in the concave part and, therefore, the electric resistance is low and the image density of the formed image is not reduced.

As described above, the resin embedded into the concave part is not likely to come off easily by external forces. Accordingly, there is no problem that the image quality of the formed image is lowered because of resin coming off from the magnetic surface being included in the toner.

Besides, the resin embedded into the concave part does not relate to charge-imparting to the toner and the resin does not come off easily. Therefore, the charge imparting effect for the carrier is not lowered when the toner is repeatedly circulated in the developing apparatus.

After the present inventors have studied the carrier, it has found that even the carrier obtained by embedding the resin into the concave part of the magnetic particles as described above can not completely prevent the occurrence of spent toner.

SUMMARY OF THE INVENTION

It is a main object of the present invention to provide an electrophotographic carrier which can more certainly prevent the occurrence of spent toner.

In order to solve the above problem, the present inventors have intensively studied about the surface state of the magnetic particles. As shown in Fig. 7, on the surface **10** of a magnetic particle **1**, a depression or concave part **11** caving in concave form from the surface **10** and a projection **12** projecting from the surface **10** are present. A peripheral part **12a** of the projection **12**, which corresponds to the junction the corner part of the projection **12** with the surface **10**, is also a place where spent toner is liable to occur, as well as the concave part **11**. Therefore, it is assumed that the occurrence of spent toner can be inhibited by using magnetic particles **1** wherein there are present a small number of the concave parts **11** and projections **12**.

However, differences in the detailed state of the magnetic particle surface, which relates to the occurrence of spent toner, can not be sufficiently distinguished by the conventional method for evaluating the surface state, such as measurement of a specific surface area.

Thus, the present inventors have studied a novel evaluation method for evaluating the surface state of the magnetic particles. As a result, it has been found that, when the magnetic particles are mixed with steel balls and fine powders of a suitable resin at 100 rpm for 4 hours, the resin is forcibly adhered to the place where spent toner is liable to occur, such as the concave parts and the projection peripheral parts of the surface of the magnetic particles. Therefore, by measuring the amount of the resin, it is possible to determine the proportion of concave parts and projections which are present on the surface of the magnetic particles.

It has also been found that by the above method (hereinafter referred to as "a method for forcibly adhering resin"), the occurrence of spent toner can be reduced or prevented with certainty if the magnetic particles have a surface state where an amount of the resin adhered to the surface of the magnetic particles (i.e. adhesion rate of the resin) is adjusted to be the range from 0.01 to 0.50%, according to a carbon content (%) measured by a carbon analyzer.

That is, the electrophotographic carrier of the present invention comprises magnetic particles having such a specific surface state that when mixing the uncoated magnetic particles with resin powder and steel balls at 100 rpm for 4 hours and then removing the steel balls and excess of resin powder, an adhesion rate of resin to the magnetic particles' surface is within the range from 0.01 to 0.50% in carbon content (%) measured by a carbon analyzer.

On the other hand, it is assumed that the occurrence of spent toner can be inhibited by coating not only the concave parts **11** shown in Fig. 7 but also the peripheral parts **12a** of the projection **12**, with the resin. The present inventors have studied a method of selectively forming a coating at the concave parts **11** and peripheral parts **12a** of the projection **12**. As a result, it has been found that the occurrence of spent toner can be inhibited or reduced when the coating containing a thermosetting resin and a thermoplastic resin is formed on the surface of the magnetic particles and then the coating is heated to a temperature higher than the melting point of the thermoplastic resin to cure the thermosetting resin.

According to the above method, the thermoplastic resin becomes liquid by heating to cure the thermosetting resin, so that the coating comprising the thermosetting resin and the thermoplastic resin formed on the surface of the magnetic particles becomes fluid. In this fluidized state, the viscosity and the surface tension of the coating increase as the curing reaction of the thermosetting resin proceeds. The coating shrinks as the surface tension increases, and then it divides into pieces and agglomerates at the position where the surface area can be reduced as much as possible, like the concave parts and the projection peripheral parts of the surface of the magnetic particles. The coating of the resin is formed at the concave parts and the projection peripheral parts when the curing reaction proceeds in this state to solidify the thermosetting resin.

Accordingly, another electrophotographic carrier of the present invention comprises magnetic particles, and a coating comprising a thermosetting resin and a thermoplastic resin, which is formed on the surface of the magnetic particles by heating to a temperature higher than a melting point of the thermoplastic resin to cure the thermosetting resin.

As described above, according to the electrophotographic toner of the present invention, the coating of the resin can be formed at the concave parts and the projection peripheral parts where spent toner is liable to occur, and therefore, the occurrence of spent toner can be reduced or prevented with certainty.

The coating of the resin formed at the projection peripheral parts is more frequently contacted with the toner than the coating in the concave parts and, therefore, has a function of charging the toner by the contact with the toner. Accordingly, the electrophotographic carrier of the present invention can also be superior in charge imparting effect of charging the toner to a conventional carrier wherein resin is embedded into the concave part of the magnetic particles.

In the electrophotographic carrier of the present invention, the coating of the resin is substantially restricted to the concave parts and the projection peripheral parts, and the magnetic particles are exposed. Therefore, the electric resistance is low and the image density of a formed image is not reduced.

Furthermore, when the coating of the resin is selectively formed at the concave parts and the projection peripheral parts of the surface of the magnetic particle having the specific surface state as described above, the occurrence of spent toner can be prevented more certainly.

Accordingly, still another electrophotographic carrier of the present invention comprises magnetic particles having such a surface state that when mixing the magnetic particles with fine powder of the resin and steel balls at 100 rpm for 4 hours and then removing the steel balls and excess fine powder of the resin having such a surface state that an adhesion rate of the resin to the magnetic particles' surface is within the range from 0.01 to 0.50% as a carbon content (%) measured by a carbon analyzer; and

a coating comprising a thermosetting resin and a thermoplastic resin, which is formed on the surface of the magnetic particles by heating to a temperature higher than the melting point of the thermoplastic resin to cure the thermosetting resin.

The electrophotographic carrier of the present invention can be superior in preventing the occurrence of spent toner, and also superior in charge imparting effect of charging the toner because the coating of the resin is selectively formed at the concave parts and the projection peripheral parts of the surface of the magnetic particles. Furthermore, the electric resistance can be low and the image density of the formed image is not detrimentally reduced.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a scanning electron micrograph illustrating a particle structure of the carrier of Example 1.
Fig. 2 is a scanning electron micrograph illustrating a particle structure of the carrier of Example 2.
Fig. 3 is a scanning electron micrograph illustrating a particle structure of the carrier of Comparative Example 1.
Fig. 4 is a scanning electron micrograph illustrating a particle structure of the carrier of Example 4.
Fig. 5 is a scanning electron micrograph illustrating a particle structure of the carrier of Example 5.
Fig. 6 is a scanning electron micrograph illustrating a particle structure of the carrier of Example 6.
Fig. 7 is a schematic section illustrating the surface of the magnetic particles.

DETAILED DESCRIPTION OF THE INVENTION

Firstly, the electrophotographic carrier comprising magnetic particles having a surface state that an adhesion rate of a resin due to the method for forcibly adhering resin is within the range from 0.01 to 0.50% will be described.

Examples of magnetic particles constituting the electrophotographic carrier of the present invention include particles of iron, iron subjected to an oxidation treatment, reduced iron, magnetite, copper, silicon steel, ferrite, nickel and cobalt; particles of alloys comprising the above materials and other material such as manganese, zinc and aluminum; particles wherein fine powders of each of the above materials are dispersed in a binding resin; particles of ceramics such as titanium oxide, aluminum oxide, copper oxide, magnesium oxide, lead oxide, zirconium oxide, silicon carbide, magnesium titanate, barium titanate, lithium titanate, lead titanate, lead zirconate and lithium niobate; particles of high dielectric constant substances such as ammonium dihydrogen phosphate ($NH_4H_2PO_4$), potassium dihydrogen phosphate (KH_2PO_4) and Rochelle salt.

The method for forcibly adhering resin for defining the surface state of the above magnetic particles will be described.

Non-coated magnetic particles and powder of a suitable resin (e.g. styrene-acrylic resin which is the same as a fixing resin for toner) having a mean diameter of 8 to 10 μm, are mixed together with steel balls, such as stainless steel balls, having a mean diameter of 7.5±0.5μm, at 100 rpm for 4 hours.

More specifically, 40g of a mixture of magnetic particles and resin powder in which the proportion of magnetic particle is 4.5 % by weight, and 40 steel balls are poured into a 300-ml plastic container and then mixed.

The mixing time may be over 4 hours. When the mixing time is less than 4 hours, there is a possibility that fusing of the resin is imperfect and the measured value of the adhesion rate of the resin is smaller than an actual value.

Then, the mixture obtained by removing the steel balls is placed on a sieve of 400 mesh and the fine powders of the excess resin is removed by blowing air to obtain a sample of the magnetic particles to which the resin is adhered.

The carbon content (%) of this sample is measured by a carbon analyzer, and the adhesion rate is calculated based on the resin used.

The magnetic particles having a smaller adhesion rate of the resin than the above range, have a small number of the concave parts and the projections, and the surface is too smooth, which results in decrease in surface area of the carrier. Therefore, the charge imparting effect for charging the toner is insufficient.

To the contrary, in the magnetic particles whose adhesion rate of the resin exceeds the above range, since there are too many concave parts and projections, spent toner occurs in a very short period when mixing with the toner. Therefore, uniform charging cannot be obtained and the charge imparting effect for charging the toner is lowered. As a result, fog might occur in a formed image, toner scattering might occur or the transfer efficiency of the toner is lowered.

The adhesion rate of the resin to the magnetic particle is preferably from about 0.10 to about 0.45%.

In order to prepare the magnetic particles having a surface state that the adhesion rate of the resin is within the above range, various methods can be used. For example, when the magnetic particles are produced by sintering a magnetic material, the crystal growth of the magnetic particles is promoted as the sintering temperature is increased, so that the surface of the particles is apt to be smooth to reduce the number of the concave parts and the projections. Accordingly, the sintering condition may be adjusted to prepare magnetic particles having a surface state that the adhesion rate of the resin is within the above range.

Considering that the magnetic particles are used for a normal image forming apparatus, the particle size of the magnetic particles may be the same as that of a conventional carrier, and it is normally about from 10 to 200 μm, preferably about from 30 to 150 μm.

Considering that the magnetic particles are used for a normal image forming apparatus, the saturation magnetization of the magnetic particles may be the same as in conventional carriers, and it is preferably about from 35 to 70 emu/g.

The magnetic particles can be sufficiently used as they are, as an electrophotographic carrier. The coating of a resin may be formed on the whole surface of the magnetic particles for the purpose of controlling the charged amount and charged polarity of the toner, improving the humidity dependence, preventing the occurrence of spent toner and improving the fluidity.

As the resin for coating the whole surface of the magnetic particles, there can be used various thermoplastic or thermosetting resins which have hitherto been known.

In order to form the coating of the resin on the whole surface of the magnetic particles, a coating solution prepared by dissolving the resin in a suitable solvent may be applied on the surface of the magnetic particles, followed by drying. As a method of applying the above coating solution on the surface of the magnetic particles, there can be used various conventional methods, for example,

(a) a mechanical mixing method comprising uniformly mixing the magnetic particles with a coating solution,
(b) a spraying method comprising spraying a coating solution to the magnetic particles,
(c) a dipping method comprising dipping the magnetic particles in a coating solution,
(d) a fluidized bed method in which a coating solution is sprayed to magnetic particles maintained in a floating/fluidized state using a fluidized bed, and
(e) a tumbling bed method in which a magnetic carrier in tumbling state is brought into contact with a coating solution.

When the resin is a thermosetting resin, a coated and dried film may be heated in an electric furnace or the like.

To the coating of the resin, additives (e.g. carbon black, a fatty acid metal salt) which adjust characteristics of the coating of the resin (particularly, the charge imparting property to the toner) or various stabilizers may be optionally blended in small amounts.

The following is a description of the electrophotographic carrier, wherein the coating comprising a thermosetting resin and a thermoplastic resin is formed on the surface of the magnetic particles and then the coating is heated to a temperature higher than the melting point of the thermoplastic resin to cure the thermosetting resin, thereby forming the coating of the resin at the concave parts and projection peripheral parts of the magnetic particles' surface.

The coating area (%) of the resin in the electrophotographic carrier is not specifically limited, but preferably within the range from 0.1 to 60%, more preferably from 5 to 50%.

When the coating area of the coating of the resin is below the above range, the charge imparting effect for charging the toner is likely to be insufficient. On the other hand, when the coating area exceeds the above range, the exposed area of the magnetic particle is small. As a result, there is a possibility that the electric resistance of the carrier increases to reduce the image density of a formed image.

As the magnetic particles, there can be used the same ones as described above. In the carrier coated with the resin in the aforesaid manner, however, the adhesion rate of the resin due to the method for forcibly adhering resin is not limited to the above range.

As the thermosetting resin contained in the coating which is formed on the surface of the magnetic particles in order to coat the concave parts and projection peripheral parts of the magnetic particles' surface with the resin, examples are silicone resin, various modified silicone resins, curable acrylic resin, copolymer of curable acrylic resin and styrene, unsaturated polyester resin and amino resin. These can be used alone or in any combination thereof.

As the thermoplastic resin contained in the coating, together with the thermosetting resin, examples are acrylic resin, styrene-acrylic resin and saturated polyester resin. These can be used alone or in any combination thereof.

It is preferred that the thermosetting resin and the thermoplastic resin are of the same system in view of integrity of the coating, but resins of different systems may be used if both have good compatibility.

The mixing ratio (i.e, weight ratio, R/D) of the thermosetting resin (hereinafter referred to as "R") to the thermoplastic resin (hereinafter referred to as "P") is preferably from 95.5/0.5 to 51/49, more preferably from 99/1 to 90/10.

When the ratio R/P deviates from the above range in the direction that the proportion of the thermoplastic resin is smaller than the above range, the effect of maintaining the coating in the fluidized state on curing of the thermosetting resin may be insufficient, the coating might not condense satisfactorily at the concave parts and the projection peripheral parts of the surface of the magnetic particles. On the other hand, when the ratio R/P deviates from the above range in the direction that the proportion of the thermoplastic resin is larger than the above range, it is liable that the effect of imparting charging properties to the toner is enhanced to reduce the image density of the formed image.

In order to form the coating comprising the thermosetting resin and the thermoplastic resin on the surface of the magnetic particles, a coating solution prepared by dissolving both resins in a suitable solvent may be applied on the surface of the magnetic particles, followed by drying. As the method of applying the above coating solution on the surface of the magnetic particles, there can be used various conventional applying methods such as those shown in the items (a) to (e) as previously described.

In order that the magnetic particles on which the coating is formed by applying the coating solution, followed by drying, are heated to a temperature higher than the melting point of the thermoplastic resin to cure the thermosetting resin, for example, heat treatment using an electric furnace can be used.

To the coating of the resin, additives (e.g. carbon black, a fatty acid metal salt) which adjust characteristics (particularly, charge imparting properties to the toner) of the coating of the resin, and various stabilizers may be optionally blended in small amounts.

The method in which the coating is selectively formed at the concave parts and the projection peripheral parts of the surface of the magnetic particles by heating the coating comprising a thermosetting resin and a thermoplastic resin to a temperature higher than the melting point of the thermoplastic resin to cure the thermosetting resin, is applicable to the magnetic particles having a surface state that a specific adhesion rate due to the method for forcibly adhering resin is within the above range.

In the electrophotographic carrier, the occurrence of spent toner can be prevented more certainly by combining the effect obtained by using magnetic particles whose adhesion rate of the resin due to the method for forcibly adhering resin is within the range from 0.01 to 0.50% with the effect obtained by the coating formed at the concave parts and the projection peripheral parts of the surface of the magnetic particles.

The electrophotographic carrier of the present invention is used as a two-component developer by mixing with a toner in a conventional method. The mixing ratio of the electrophotographic carrier to the toner is not specifically limited, but a concentration of the electrophotographic carrier in the developer is from 1 to 10% by weight, preferably from 2 to 8% by weight.

To the toner, external additives may be added to adjust the fluidity, charging characteristics and the like. As the external additive, there can be used various known additives, such as inorganic fine particles and fluororesin particles. Particularly, silica surface treating agents containing hydrophobic or hydrophilic silica fine particles (e.g. ultrafine particulate anhydrous silica, colloidal and silica) are suitably used.

As described above, according to the electrophotographic carrier of the present invention, the occurrence of spent toner can be reduced or prevented with certaintly by specifying the surface state of the magnetic particle with the adhesion rate of the resin due to the method for forcibly adhering resin.

It is also possible to reduce or prevent with certainty the occurrence of spent toner by forming a coating of the resin at the concave parts and the projection peripheral parts of the surface of the magnetic particles where spent toner is liable to occur. The photographic carrier is also superior in charge imparting effect for charging the toner because of the coating of the resin formed at the projection peripheral parts. Furthermore, the magnetic particles are exposed except for the concave parts and the projection peripheral parts and, therefore, the electric resistance is low and the image density of the formed image is not reduced.

The occurrence of spent toner can be more certainly prevented by specifying the surface state of the magnetic particles and coating the concave parts and the projection peripheral parts on the surface of the magnetic particles, with the resin. Such an electrophotographic carrier can also be superior in charge imparting effect for charging the toner by selectively forming the coating of the resin, and the electric resistance is low and the image density of the formed image is not detrimentally reduced.

EXAMPLES

The following Examples and Comparative Examples further illustrate the present invention.

Example 1

Copper-zinc ferrite particles having an average particle size of 80 μm, a saturation magnetization of 58 emu/g and an adhesion rate of resin due to the method for forcibly adhering resin of 0.15% were produced by sintering, and these ferrite particles were used as an electrophotographic carrier.

The surface of the resultant electrophotographic carrier was observed by a scanning electron microscope (magnification of X600). As a result, it was in a smooth state where there are present a small number of the concave parts and the projections, as shown in Fig. 1.

Example 2

Copper-zinc ferrite particles having an average particle size of 80 μm, a saturation magnetization of 58 emu/g and an adhesion rate of resin due to the method for forcibly adhering resin of 0.45% were produced by changing the sintering conditions in Example 1, and these ferrite particles were used as an electrophotographic carrier.

The surface of the resultant electrophotographic carrier was observed by a scanning electron microscope (magnification X600). As a result, there were present a lot of concave parts and projections compared with Example 1, as shown in Fig. 2.

Comparative Example 1

Copper-zinc ferrite particles having an average particle size of 80 µm, a saturation magnetization of 58 emu/g and an adhesion rate of resin due to the method for forcibly adhering resin of 0.60% were produced by changing the sintering conditions used in Example 1, and these ferrite particles were used as an electrophotographic carrier of Comparative Example 1.

The surface of the electrophotographic carrier was observed by a scanning electron microscope (magnification X600). As a result, more concave parts and projections were present than Example 2, as shown in Fig. 3.

Using the electrophotographic carriers of Examples 1 and 2 and Comparative Example 1, the following tests were conducted and their characteristics were evaluated.

(1) Practical machine test I

Each electrophotographic carrier of the Examples and Comparative Example was mixed with a toner obtained by a pulverizing method (for the electrostatic copying machine DC-2556, manufactured by Mita Industrial Co., Ltd.) to prepare a two-component developer having a toner density of 4.5% by weight. Continuous image forming (10,000 copies) was carried out, using this developer as a start developer for a modified electrostatic copying machine DC-2556 and also using the above developer as a supplementary toner.

The image density (hereinafter referred to as "ID") of an initial image and 10,000th image out of the formed images, and the fog density (hereinafter referred to as "FD") of the blank area were measured using a reflection densitometer (TC-6D, manufactured by Tokyo Denshoku Co., Ltd.).

(2) Measurement I of charged amount of toner

The charged amount (µC/g) of the toner in the developer before the continuous image forming and that after the continuous image forming of 10,000 copies were respectively measured by blow-off method.

(3) Measurement I of transfer efficiency

The transfer efficiency (%) of the toner was determined from the total consumption amount (i.e., developed amount (g)) of the toner due to the continuous image forming of 10,000 copies and the total amount of the toner (transfer residual amount (g)) recovered by the cleaning part of the image forming apparatus, according to the following equation:

Transfer efficiency (%) = Developed amount (g) - Transfer residual amount (g)/Developed amount x 100

(4) Observation I of toner scattering

After the continuous image forming of 10,000 copies, it was observed whether toner scattering occurred or not in the apparatus.

(5) Measurement I of rate of spent toner

After the continuous image forming of 10,000 copies, the developer was placed on a sieve of 400 mesh and excess toner was removed by blowing air using a blower. Then, the carbon content (%) of the recovered carrier was measured by a carbon analyzer and the measured value was taken as a rate of spent toner (%).

The above results are shown in Table 1.

Table 1

		Example 1	Example 2	Comparative Example 1
ID	Initial image	1.43	1.43	1.48
	10,000th image	1.44	1.44	1.47
FD	Initial image	0.005	0.004	0.010
	10,000th image	0.005	0.005	0.018
Charged amount (µC/g)				

Table 1 (continued)

		Example 1	Example 2	Comparative Example 1
	Before initial image	-21.5	-22.0	-18.2
	After 10,000 images	-20.4	-20.8	-15.0
Transfer efficiency (%)		75.0	74.3	45.5
Toner scattering		None	None	Observed
Rate of spent toner (%)		0.07	0.08	0.15

Example 3

4 Parts by weight of a curable styrene-acrylic resin and 1 part by weight of a methylated melamine resin, both of which are thermosetting resins, were added to 200 parts by weight of toluene, followed by mixing with stirring to prepare a coating solution for resin coating.

While maintaining 1000 parts by weight of the ferrite particles obtained in Example 2, which had an average particle size of 80 µm and a saturation magnetization of 58 emu/g and an adhesion rate of 0.45%, in a floating/fluidized state using a fluidized bed, the above coating solution was sprayed, followed by drying to form a coating on the surface of the ferrite particles.

Then, the ferrite particles were heated in an electric furnace at 200°C for one hour to cure the thermosetting resin, thereby obtaining an electrophotographic carrier.

The coating area (%) of the resin in the resultant electrophotographic carrier was measured by image analyzing method, and it was 100%.

Comparative Example 2

In the same manner as in Example 3 except for using 1000 parts by weight of the ferrite particles obtained in Comparative Example 1, which had an average particle size of 80 µm, a saturation magnetization of 58 emu/g and an adhesion rate of 0.60%, an electrophotographic carrier was obtained.

In the same manner as described above, the coating area (%) of the resin in the electrophotographic carrier was measured by the image analyzing method, and it was 100%.

The electrophotographic carriers of Example 3 and Comparative Example 2 were subjected to the above tests and their characteristics were evaluated. The results are shown in Table 2.

Table 2

		Example 3	Comparative Example 2
ID	Initial image	1.35	1.40
	10,000th image	1.34	1.48
FD	Initial image	0.002	0.003
	10,000th image	0.002	0.011
Charged amount (µC/g)			
	Before initial image	-24.6	-24.0
	After 10,000 images	-25.5	-20.3
Transfer efficiency (%)		78.9	60.2
Toner scattering		None	Observed
Rate of spent toner (%)		0.07	0.14

Example 4

3.92 Parts by weight of a styrene-acrylic resin, 0.98 parts by weight of a methylated melamine resin, both of which are thermosetting resins, and 0.1 parts by weight of a styrene-acrylic resin (melting point: 108°C) which is a thermoplastic resin, were added to 200 parts by weight of toluene, followed by mixing with stirring to prepare a coating solution for resin coating.

While maintaining 1000 parts by weight of the ferrite particles in Example 2, which had an average particle size of 80 μm, a saturation magnetization of 58 emu/g and an adhesion rate of resin of 0.45%, in a floating/fluidized state using a fluidized bed, the above coating solution was sprayed, followed by drying to form a coating on the surface of the ferrite particles.

Then, the ferrite particles were heated in an electric furnace at 200°C for one hour to cure the thermosetting resin, thereby obtaining an electrophotographic carrier.

The surface of the resultant electrophotographic carrier was observed by a scanning electron microscope (magnification of X600). As shown in Fig. 4, it was confirmed that a coating of the resin (black shadow in the figure) was formed mainly at the concave parts and the projection peripheral parts of the surface of the ferrite particle, and the coating of the resin was scarcely formed on other surface parts and projections.

The coating area (%) of the coating of the resin was measured by the image analyzing method, and it was 20%.

Example 5

In the same manner as in Example 4 except for using 1000 parts by weight of ferrite particles having an average particle size of 80 μm, a saturation magnetization of 58 emu/g and an adhesion rate of a resin of 0.52%, an electrophotographic carrier was obtained.

The surface of the resultant electrophotographic carrier was observed by a scanning electron microscope (magnification of X800). As shown in Fig. 5, it was confirmed that a coating of the resin (black shadow in the figure) was formed mainly at the concave parts and the projection peripheral parts of the surface of the ferrite particles, and the coating of the resin was scarcely formed on other surface parts and projections.

The coating area (%) of the coating of the resin was measured in the aforesaid manner, and it was 25%.

The electrophotographic carriers of Examples 4 and 5 were subjected to the above tests and their characteristics were evaluated. The results are shown in Table 3.

Table 3

		Example 4	Example 5
ID	Initial image	1.46	1.43
	10,000th image	1.44	1.46
FD	Initial image	0.001	0.004
	10,000th image	0.002	0.005
Charged amount (μC/g)	Before initial image	-22.4	-20.8
	After 10,000 images	-22.8	-20.3
Transfer efficiency (%)		82.3	72.3
Toner scattering		None	None
Rate of spent toner (%)		0.04	0.08

Example 6

3.92 Parts by weight of an acrylic-modified silicone resin, 0.98 parts by weight of a melamine resin, both of which are thermosetting resins, and 0.1 parts by weight of a styrene-acrylic resin (melting point: 108°C) which is a thermoplastic resin were added to 200 parts by weight of toluene, followed by mixing with stirring to prepare a coating solution for resin coating.

While maintaining 1000 parts by weight of copper-zinc ferrite particles produced by sintering, which had an average particle size of 60 μm, a saturation magnetization of 57 emu/g and a surface state that an adhesion rate of the resin is 0.3%, in a floating/fluidized state using a fluidized bed, the above coating solution was sprayed, followed by drying to form a coating of the above respective resins on the surface of the ferrite particles.

Then, the ferrite particles were heated in an electric furnace at 200°C for one hour to cure the thermosetting resin, thereby obtaining an electrophotographic carrier.

The surface of the resultant electrophotographic carrier was observed by a scanning electron microscope (magnification X1000). As shown in Fig. 6, it was confirmed that a coating of the resin (black shadow in the figure) was formed mainly at the concave parts and the projection peripheral parts of the surface of the ferrite particles, and the coating of the resin was scarcely formed on other surface parts and projections.

The coating area (%) of the coating of the resin was measured by the aforesaid method, and it was 18.5%.

The electrophotogaphic carrier of Example 6 was subjected to the above tests and its characteristics were evaluated. The results are shown in Table 4.

Table 4

		Example 6
ID	Initial image	1.40
	10,000th image	1.42
FD	Initial image	0.001
	10,000th image	0.001
Charged amount (μC/g)		
	Before initial image	-23.3
	After 10.000th image	-23.8
Transfer efficiency (%)		83.4
Toner scattering		None
Rate of spent toner (%)		0.02

The electrophotographic carrier of Example 6 was subjected to the following tests and its characteristics were evaluated.

(1) Practical machine test II

Each electrophotographic carrier of the Examples was mixed with a toner obtained by pulverizing method (for the electrostatic copying machine A2-ZS, manufactured by Mita Industrial Co., Ltd.) to prepare a two-component developer having a toner density of 6% by weight. Continuous image forming of 30,000 copies was carried out, using this developer as a start developer in a modified electrostatic copying machine A2-ZS and using the above developer as a supplementary toner.

The image density (ID) of the initial image, 15,000th image and 30,000th image out of the formed images, and the fog density (FD) of the blank area were measured by using a reflection densitometer (TC-6D, manufactured by Tokyo Denshoku Co., Ltd.).

(2) Measurement II of charged amount of toner

The charged amount (μC/g) of the toner in the developer before the continuous image forming, that after the continuous image forming of 15,000 copies and that after the continuous image forming of 30,000 copies were respectively measured by blow-off method.

(3) Measurement II of transfer efficiency

The transfer efficiency (%) of the toner was determined from the total consumption amount of the toner (developed amount (g)) due to the continuous image forming of 30,000 copies and total amount of the toner (transfer residual amount (g)) recovered by the cleaning part of the image forming apparatus, according to the above equation.

(4) Observation II of toner scattering

After the continuous image forming of 30,000 copies, it was observed whether toner scattering occurred or not in the apparatus.

(5) Measurement II of rate of spent toner

After the continuous image forming of 30,000 copies, the developer was placed on a sieve of 400 mesh and excess toner was removed by blowing air using a blower. Then, the carbon content (%) of the recovered carrier was measured by a carbon analyzer and the measured value was taken as a rate of spent toner (%).

The above results are shown in Table 5.

Table 5

		Example 6
ID	Initial image	1.446
	15,000th image	1.425
	30,000th image	1.446
FD	Initial image	0.002
	15,000th image	0.004
	30,000th image	0.003
Charged amount (μC/g)		
	Before initial image	-28.1
	After 15,000 images	-21.4
	After 30,000 images	-22.1
Transfer efficiency (%)		83.7
Toner scattering		None
Rate of spent toner (%)		0.037

Claims

1. Magnetic particles for use in manufacture of an electrophotographic carrier, the magnetic particles having such a specific surface state that when mixing the magnetic particles with resin powder and steel balls at 100 rpm for 4 hours and then removing the steel balls and excess of resin powder, an adhesion rate of a resin to the magnetic particles' surface is within the range from 0.01 to 0.50% in carbon content (%) measured by a carbon analyzer.

2. Magnetic particles according to claim 1, wherein the surface of the magnetic particles having the surface state as represented by the adhesion rate of the resin is coated with a resin.

3. An electrophotographic carrier comprising magnetic particles and a coating comprising a thermosetting resin and a thermoplastic resin, which is formed on a surface of the magnetic particles by heating to a temperature higher than the melting point of the thermoplastic resin to cure the thermosetting resin.

4. An electrophotographic carrier according to claim 3, wherein the coating of the resin is formed at least at concave parts and projection peripheral parts of the surface of the magnetic particles.

5. An electrophotographic carrier according to claim 4, wherein the coating area (%) of the resin on the surface of the magnetic particles is within the range from 0.1 to 60%.

6. An electrophotographic carrier comprising magnetic particles having the surface state as defined in claim 1, and a coating comprising a thermosetting resin and a thermoplastic resin, which is formed on the surface of the magnetic particles by heating to a temperature higher than the melting point of the thermoplastic resin to cure the thermosetting resin.

7. A method of manufacture of an electrophotographic carrier, in which magnetic particles are mixed with resin powder and steel balls at 100 rpm for 4 hours, the steel balls and excess resin powder are removed, and resin-coated magnetic particles are obtained in which the adhesion rate of the resin to the magnetic particles' surface is within the range from 0.01 to 0.50% in carbon content (%) measured by a carbon analyzer.

Fig. 1

Fig. 2

Fig. 3

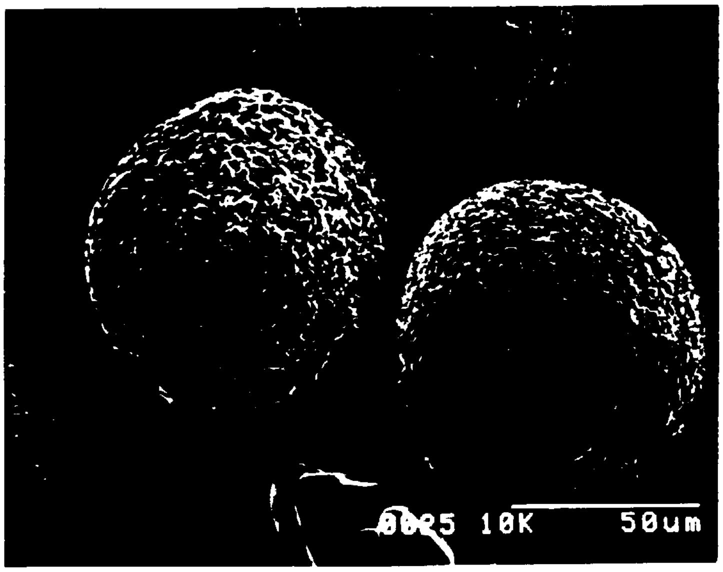

Fig. 4

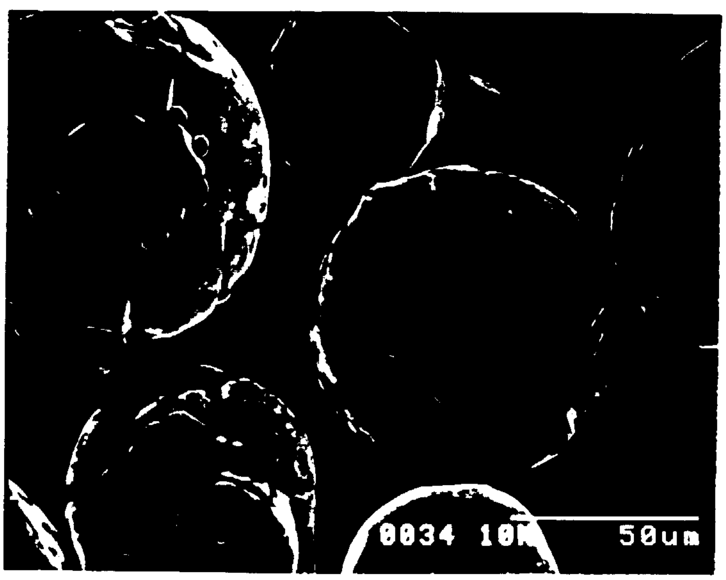

Fig. 5

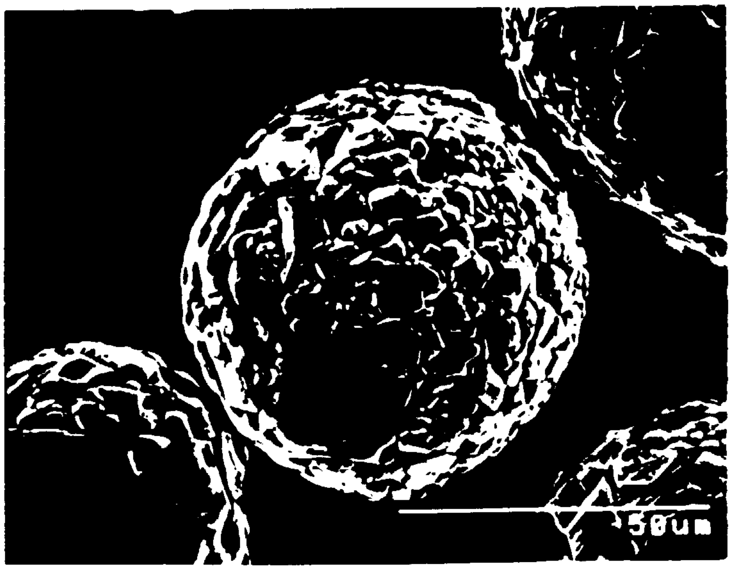

Fig. 6

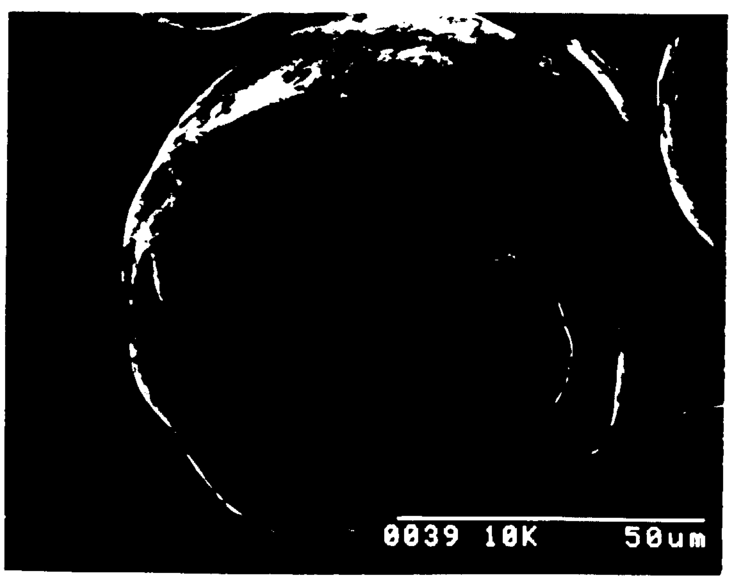

Fig. 7