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㉙ **Carrier for electrostatic image development and method of preparing it.**

㉚ A carrier for an electrostatic image development comprising magnetic material particles covered with resin particles is disclosed. The carrier is prepared by applying a repeated impact force at a material temperature within the range of from 50 to 110 °C to a mixture of magnetic material particles having a weight mean particle diameter of from 10 to 200 μm and resin particles having a weight mean particle diameter of less than 1/200 of that of the magnetic material particles.

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CARRIER FOR ELECTROSTATIC IMAGE DEVELOPMENT AND METHOD OF PREPARING IT

FIELD OF THE INVENTION

The present invention relates to a carrier for electrostatic image development, used in electrophotography, electrostatic recording and electrostatic printing.

BACKGROUND OF THE INVENTION

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In general, in the electrophotography, a toner image is formed by applying uniform electrostatic charges to a latent image supporting member, i.e., a photosensitive member, having a photosensitive layer comprising a photoconductive material, followed by imagewise exposure to form an electrostatic latent image on the surface of the photosensitive member, and developing the electrostatic latent image with a developer. The toner image thus formed is transferred to a transferring medium such as paper, and fixed thereon by heating or application of pressure to form a copy image.

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Known as methods of developing the electrostatic latent image are wet developing and dry developing. Known as developers used in the latter dry developing are, in general, a one-component developer comprised of only a magnetic toner which comprises a toner containing a magnetic material, and a two-component developer comprised of a non-magnetic toner containing no magnetic material and a carrier having magnetic properties.

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The latter two-component developer, in which the toner and carrier are mechanically agitated so that the toner may be frictionally charged, enables considerably easy control of the charging polarity and amount of electrostatic charging of the toner by the selection of properties of the carrier and conditions for the agitating. It also allows a wide range for the selection of the colors that can be imparted to the toner. Thus, in view of these, the latter developer is more advantageous than the former one-component developer.

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As the carrier used in the two-component developer, a coated carrier comprising magnetic particles whose surfaces are coated with a resin has been used with appreciation because of the possibility of improving the durability of carriers, frictional electrostatic charging performance and so forth.

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Most widely used as such a coated carrier is a spray-coated carrier obtained by spray-coating in a fluidized bed the surfaces of magnetic particles with a coating solution prepared by dissolving a coating resin in a solvent, followed by drying.

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In the technique of the above spray coating, however, the carrier particles may be mutually fused because of the solvent used, so that the carrier may have a large diameter, resulting in a great decrease in the yield of the carrier having the desired particle size distribution. It also requires a drying step, and also requires a reasonably long period of time for the manufacture of the carrier, bringing about the problem of a low productivity. The productivity may be further lowered with an increase in the coverage with resin and a decrease in the diameter of magnetic particles. To cope with this problem, the following countermeasures may be taken as a means for improving the productivity as a result of the shortening of time:

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- (i) to increase the concentration of the coating resin in the coating solution; or
- (ii) to increase the number of spray nozzles.

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In the case of the above (i), however, the coating solution, when adhered to the particles of the magnetic material, may not smoothly spread because of its high viscosity, only providing an uneven coating, resulting in a lowering of the durability of carrier. The particles of the magnetic material may also readily adhere and fuse to each other once they have come into contact, resulting in a great decrease in the yield of the carrier.

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In the case of the above (ii), there is a limit in increasing the number of spray nozzles, and moreover an increase in the quantity of the coating solution sprayed at one time may result in an increase in the rate of fusion of the magnetic material particles, bringing about the same problem as in the first-mentioned case. On the other hand, in order to prevent the fusion, a technique is available in which a mechanism, called agitator, for imparting a shear force is equipped in the fluidized bed. This, however, may bring about a coarse and non-uniform state on the surfaces as a result of the compulsory disintegration of fused products with use of the agitator, resulting in a lowering of the durability of the carrier.

In addition, the spray coating takes a long time for the coating, and requires the recovery and thermal

disposal of the solvent, making the manufacture uneasy.

It also requires the solubility to solvent of the resin that forms a coating layer, making narrow the range of selecting the resin and bringing about an obstacle to the selection of resins having good film-forming properties.

5 Another problem is that fine holes are produced on the surface of the carrier when the solvent is evaporated, resulting in non-uniformity on the surface of the carrier. The fusion also tends to take place to make it difficult to obtain a carrier with the particle size fitted to the purpose, also resulting in a poor yield.

Still another problem is that part of starting materials scattered as a result of spraying does not participate in the formation of a layer, so that the starting materials are wasted and the materials which are
10 nor coated electrostatically adhere in the form of powder to the surface of the carrier to give ill influences in carrying out the developing.

On the other hand, coating techniques that do not rely on the spray coating have been developed, see Japanese Patent Publications Open to Public Inspection (hereinafter referred to as Japanese Patent O.P.I. Publications) No. 35735/1979, No. 118047/1980, No. 37358/1988, No. 37359/1988 and No. 37360/1988.

15 The coating disclosed in these publications comprises mixing a carrier core material and polymer fine particles by a mechanical means to electrostatically interlockingly cover the surface of the carrier core material with the polymer fine particles to form a covering, and thereafter fixing said polymer fine particles by melting them by heat or dissolving them using a solvent, thereby covering the surface of the carrier core material with a resin layer.

20 In the above coating techniques, however, the resin interlockingly covering the core material is melted in fixing the polymer fine particles, so that the resin particles may adhere to each other or core particles may adhere and fuse to each other through the resin particles, bringing about the problem that the yield to obtain a carrier with the desired particle size distribution is lowered.

Another problem is that it takes much time for a cooling step since the surface of the core material is
25 covered with the resin layer at temperatures close to the melting point or not lower than the melting point, and a disintegrating step is further required to loosen blocked coated carrier particles to separate them into unblocked carrier particles, resulting in a serious lowering of the production efficiency.

Since the resulting carrier is coated with the resin in part, there is still another problem that the carrier has a poor electrostatic charging stability at a high temperature and high humidity compared with a carrier
30 entirely coated with a resin.

Moreover, the resin may undergo a change in properties because the core material is covered with the resin layer at temperatures close to, or not lower than, the melting point of the resin, and hence an inert atmosphere that may not cause the change in properties must be provided, making production apparatus
very complicated.

35 On the other hand, in the instance where the resin with which the core material is interlockingly covered is melted using a solvent, the resin must be selected in a narrow range like the case of the spray coating mentioned above. There also are the problems of the recovery and thermal disposal of solvents, the fusion, and so forth.

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SUMMARY OF THE INVENTION

45 A first object of the present invention is to provide a carrier for electrostatic image development, that enables selection in a wide range, of the resin constituting the resin coating, and also enables firm fixing of the resin coating, may cause film peeling with difficulty, and is durable, having stable properties of imparting electrostatic charge.

A second object of the present invention is to provide a method of preparing a carrier for electrostatic image development, that does not require any treatment for the recovery of solvents, can prepare the
50 carrier through a simple means in a short time, and yet may cause fusion or fine holes with difficulty and can obtain in a high yield a carrier having the desired particle size distribution.

A third object of the present invention is to provide a carrier for electrostatic image development, that may generate less out-of-coating matters which do not contribute the coating, and hence can prevent difficulties caused by adhesion of the out-of-coating matters on the carrier surface as a result of their
55 liberation.

A fourth object of the present invention is to provide a method of preparing a carrier for electrostatic image development, that requires no disintegrating step, and can prepare the carrier through a simple means in a short time and yet in a high yield.

A fifth object of the present invention is to provide a carrier for electrostatic image development, that can achieve a stable electrostatic charging performance even at a high temperature and high humidity, and is free from environment dependence.

The objects described above can be achieved by a method of preparing a carrier for electrostatic image development, comprising forming a uniform mixture comprised of magnetic material particles having a weight mean particle diameter of from 10 to 200 μm and resin particles having a weight mean particle diameter of less than 1/200 of that of said magnetic material particles, and repeatedly applying an impact force to said mixture in a mixing vessel having a material temperature set within the range of from 50 to 110°C, thereby coating said magnetic material particles with the resin material of said resin particles, and a carrier for electrostatic image development, prepared according to said method.

In an embodiment of the present invention, said magnetic material particles may preferably have a circularity of not less than 0.7. The resin particles may also preferably have a BET specific surface area within the range of from 40 m^2/g to 6,000 m^2/g .

The carrier for electrostatic image development, according to the present invention can be prepared through a simple means in a short time and yet in a high yield, and has a superior durability, exhibiting a stable frictional electrostatic charging performance.

More specifically, the carrier can be obtained according to dry coating, using the magnetic material particles and resin particles both having a specific particle diameter, so that;

- i) no treatment such as washing or drying is required and the time taken for the coating can be greatly shortened;
- ii) the rate of fusion is so small that the carrier with a particle size distribution corresponding with the magnetic material particles can be obtained in a high yield;
- iii) any treating equipment such as solvent-recovering apparatus or solvent-burning apparatus is not required, and hence the production cost can be decreased;
- iv) the coating of the magnetic material particles with the resin particles can be achieved in an increased efficiency, and hence the starting materials can be efficiently utilized;
- v) the resin particles adhere and spread on the surfaces of the magnetic material particles, and therefore the peel resistance and durability can be superior and a stable frictional electrostatic charging performance can be exhibited;
- vi) it becomes possible to use even a resin slightly soluble in a solvent, and hence the resin can be selected in a greatly expanded range to make it possible to obtain a coated carrier having various properties; and
- vii) because of entire coating of the carrier surface with the coating resin, stable frictional electrostatic charging performance can be exhibited even at a high temperature and high humidity, and hence a coated carrier free from any environment dependence can be obtained.

DETAILED DESCRIPTION OF THE INVENTION

The present invention will be described below in a specific manner.

In a preferred embodiment of the present invention, magnetic material particles having a weight mean particle diameter of from 10 to 200 μm and a circularity of not less than 0.7, and resin particles having a weight mean particle diameter within the range of from 1/2,000 to 1/200 of that of said magnetic material particles and a BET specific surface area within the range of from 40 m^2/g to 6,000 m^2/g are mixed and stirred to be brought into a uniformly mixed state, and an impact force is repeatedly applied to the resulting mixture. As a result, the resin particles are spread and adhered on the surfaces of the magnetic material particles. A coated carrier can be thus prepared.

Regarding the mixing weight ratio of the magnetic material particles to the resin particles, the resin particles may be used in an amount of from 0.1 to 10 parts by weight, and preferably from 0.5 to 4 parts by weight, based on 100 parts by weight of the magnetic material particles.

The impact force applied to the mixture comprising the magnetic material particles and resin particles may be satisfactory if it is of the strength to the extent that the magnetic material particles are not crushed to powders.

Regarding the weight mean particle diameter of from 10 to 200 μm as defined for the magnetic material particles, a size less than the lower limit results in an excessively small diameter of the resulting coated carrier, tending to cause adhesion of the carrier on a photosensitive member, resulting in a deterioration of image quality.

On the other hand, a size more than the upper limit results in an excessively large diameter of the resulting coated carrier, making it necessary to make severe control of toner concentration in order to impart appropriate frictional electrostatic charging to the toner, which requires an expensive toner concentration control system. It also becomes difficult to make the coated carrier supported on a developer supporting member in a uniform and high density. As a result, the quantity of the toner adhered to the carrier and conveyed to a developing space becomes inconstant to cause deterioration of the development performance and image quality.

As materials for the magnetic material particles, it is preferred to use substances capable of being strongly magnetized in the corresponding direction as a result of application of a magnetic field, as exemplified by metals such as iron, nickel and cobalt that show ferromagnetism, including iron, ferrites and magnetites, or alloys or compounds containing any of these metals.

The ferrites herein generically refer to magnetic oxides containing iron, including a ferrite represented by the chemical formula: $MO \cdot Fe_2O_3$. In the chemical formula, M represents a divalent metal, and specifically represents nickel, copper, zinc, manganese, magnesium, lithium, or the like.

The magnetic material particles may preferably have a circularity of not less than 0.7. Use of the magnetic material particles having such a high circularity brings about a high circularity also in the resulting coated carrier to increase the fluidity of the carrier. As a result, it becomes possible to steadily convey an appropriate quantity of toner to the developing space, so that a much superior development performance can be exhibited.

Herein, the circularity refer to what is defined by the following formula:

$$\text{Circularity} = \left(\frac{\text{Peripheral length of a circle having the same area as the projected area of a particle}}{\text{Length of the contour of the projected image of the particle}} \right)^2$$

This circularity can be measured, for example, with an image analyzer (a manufacture of Nippon Abionics Co.).

The weight mean particle diameter of the resin particles may be within the range of from 1/20,000 to 1/200, and preferably from 1/2,000 to 1/400, relative to that of the magnetic material particles. From a practical viewpoint, however, used are resin particles having a weight mean particle diameter of from 0.001 to 1 μm , and preferably from 0.01 to 0.15 μm , and a BET specific surface area of from 40 m^2/g to 6,000 m^2/g . A weight mean particle diameter more than 1.0 μm or a BET specific surface area of less than 40 m^2/g , of the resin particles makes the resin particles spread with difficulty on the surface of the magnetic material particles, resulting in a difficulty in the coating treatment under dry conditions. A weight mean particle diameter less than 0.01 μm or a BET specific surface area more than 6,000 m^2/g may worsen the dispersibility, sometimes making it impossible to achieve uniform coating, also sometimes resulting in a lowering of the yield.

There are no particular limitations on the materials for the resin particles, and various resins can be used. Namely, in the present invention, the dry coating of a non-solvent type can be employed and resins slightly soluble to solvents can also be used, so that the resins can be selected in a reasonably wide range. To describe specifically, it is possible to use resins as exemplified by styrene resins, acrylic resins, styrene-acrylic resins, vinyl resins, ethylene resins, rosin modified resins, polyamide resins, polyester resins, silicone resins, and fluorine resins. These resins may be used in combination.

Of these, styrene-acrylic resins and acrylic resins can be particularly preferably used. This styrene-acrylic resins are resins obtained by copolymerization of styrene monomers with acrylic monomers. Specific examples of the styrene monomers may include, for example, styrene, o-methylstyrene, m-methylstyrene, p-methylstyrene, α -methylstyrene, p-ethylstyrene, 2,4-dimethylstyrene, p-butylstyrene, p-t-butylstyrene, p-hexylstyrene, p-octylstyrene, p-nonylstyrene, p-decylstyrene, p-dodecylstyrene, p-methoxystyrene, p-phenylstyrene, p-chlorostyrene, and 3,4-dichlorostyrene. These monomers may be used alone or in combination of plural ones.

Specific examples of the acrylic monomers may include, for example, acrylic acids or esters thereof such as acrylic acid, methyl acrylate, ethyl acrylate, butyl acrylate, isobutyl acrylate, propyl acrylate, octyl acrylate, dodecyl acrylate, lauryl acrylate, 2-ethylhexyl acrylate, stearyl acrylate, 2-chloroethyl acrylate, phenyl acrylate, and methyl α -chloroacrylate; methacrylic acids or esters thereof such as methacrylic acid, methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, isobutyl methacrylate, octyl methacrylate, dodecyl methacrylate, lauryl methacrylate, 2-ethylhexyl methacrylate, stearyl methacrylate, phenyl methacrylate, dimethylaminoethyl methacrylate, and diethylaminoethyl methacrylate; and others. These monomers may be used alone or in combination of plural ones.

In obtaining the above styrene-acrylic resins, the styrene monomers and acrylic monomers may preferably be in a compositional ratio of from 9:1 to 1:9 in weight ratio. The styrene component can afford to harden coating films and the acrylic component can afford to toughen coating films. The amount of the electrostatic charging attributable to the toner in the frictional electrostatic charging between the coated carrier and toner can also be controlled to a considerable extent by appropriately varying the compositional ratio of these components.

The carrier may preferably have a weight mean particle diameter within an appropriate range corresponding with that of the magnetic material particles. That is to say, an excessively small weight mean particle diameter of the carrier tends to cause adhesion of the carrier on the photosensitive member, resulting in a deterioration of image quality. On the other hand, an excessively large weight mean particle diameter thereof results in a small specific surface area, so that it becomes difficult to achieve appropriate frictional electrostatic charging of the toner. It also becomes difficult for the carrier to be supported on the developer supporting member in a uniform state and also in a high density, resulting in a poor development performance.

To obtain a carrier having all the required properties, it is preferable for the carrier to have a narrow particle size distribution.

The weight mean particle diameter ($\bar{r}_w$) of the magnetic material particles is a value measured using "Microtruck, Type 7981-OX", manufactured by Lees & Northrup Co.; and the weight mean particle diameter ($\bar{r}_w$) of the resin particles, measured using "Coulter, Model N4 Series", manufactured by Coulter Electronics Co.

The carrier for electrostatic image development according to the present invention can be prepared, for example, by the following procedure:

The magnetic material particles having a weight mean particle diameter of from 10 to 200 μm , and resin particles having a weight mean particle diameter of less than 1/200 of that of said magnetic material particles and a BET specific surface area within the range of not less than 40 m^2/g are mixed and stirred using, for example, an ordinary stirring apparatus until they are uniformly mixed. The resulting mixture is poured into, for example a high speed stirring mixing vessel or the like set to have a material temperature within the range of from 50 to 110 $^\circ\text{C}$, and an impact force is repeatedly applied to the above mixture for 10 to 60 minutes, and preferably 15 to 30 minutes. As a result, the resin particles are spread and adhered on the surfaces of the magnetic material particles. A coated carrier can be thus obtained.

In the above, an excessively high material temperature may make higher the adhesion of the resin particles, so that a phenomenon may be caused in which the particles of the resin particle powder are agglomerated each other into a mass and also the magnetic material particles may be combined through the resin particles to cause fusion. This makes it difficult to uniformly adhere the resin particles to the surfaces of the magnetic material particles.

EXAMPLES

The present invention will be described below by giving Examples, but the present invention is by no means limited to these. In the following, "parts" is by weight.

(Preparation of toner)

Using a ball mill, 100 parts of polyester resin, 10 parts of carbon black and 3 parts of a low molecular weight polypropylene were mixed, followed by kneading, pulverization and classification to obtain a toner with an average particle diameter of 11 μm .

(Preparation of developer)

A carrier prepared in each Example and Comparative Example and the above toner particles were mixed so that the content of the toner particles may become appropriate corresponding with the particle diameter of the following each carrier. Electrostatic latent image developers were thus prepared.

(Preparation of carrier)

Example 1	
Cu-Zn-based ferrite carrier (weight mean particle diameter $\bar{r}_w$: 80 μm)	5,000 parts
Methyl methacrylate/butyl methacrylate copolymer (weight compositional ratio: 8/2; $\bar{r}_w$: 0.06 μm)	100 parts

The above materials were mixed for 15 minutes using a high speed stirring mixing vessel to prepare an ordered mixture. Thereafter, hot water was circulated in the above mixing vessel, the material temperature was set to 70 °C, and the main stirring blade was rotated to carry out coating for 15 minutes. A coated carrier was thus obtained.

In Examples and Comparative Example set out in the following, Example 1 was repeated under the same conditions to obtain coated carriers, except that the conditions as picked out and set out below were changed.

Example 2	
Cu-Zn-based ferrite carrier ($\bar{r}_w$: 100 μm)	5,000 parts
MMA/BMA (8/2)* ($\bar{r}_w$: 0.06 μm)	75 parts

* methyl methacrylate/butyl methacrylate (8/2) copolymer

Example 3	
Iron powder carrier ($\bar{r}_w$: 100 μm)	5,000 parts
MMA/BMA (8/2) ($\bar{r}_w$: 0.06 μm)	60 parts

Example 4	
Mg-Cu-Zn-based ferrite carrier ($\bar{r}_w$: 45 μm)	5,000 parts
MMA/BMA (8/2) ($\bar{r}_w$: 0.06 μm)	125 parts

Example 5	
Cu-Zn-based ferrite carrier ($\bar{r}$ w: 80 μm)	5,000 parts
MMA/BMA (8/2) ($\bar{r}$ w: 0.10 μm)	100 parts

Example 6	
Mg-Cu-Zn-based ferrite carrier ($\bar{r}$ w: 45 μm)	5,000 parts
MMA/BMA (8/2) ($\bar{r}$ w: 0.10 μm)	125 parts

Example 7	
Cu-Zn-based ferrite carrier ($\bar{r}$ w: 25 μm)	5,000 parts
MMA/BMA (8/2) ($\bar{r}$ w: 0.06 μm)	175 parts

Example 8	
Cu-Zn-based ferrite carrier ($\bar{r}$ w: 80 μm)	5,000 parts
MMA/St* (6/4) ($\bar{r}$ w: 0.075 μm)	100 parts

* styrene

Example 9	
Cu-Zn-based ferrite carrier ($\bar{r}$ w: 80 μm)	5,000 parts
Silicone fine particles ($\bar{r}$ w: 0.1 μm)	100 parts

Example 10	
Cu-Zn-based ferrite carrier ($\bar{r}$ w: 80 μm)	5,000 parts
Ethylene tetrafluoride resin fine particles ($\bar{r}$ w: 0.2 μm)	150 parts

Example 11	
Cu-Zn-based ferrite carrier ($\bar{r}w$: 80 μm)	5,000 parts
Trichloromethyl methacrylate resin fine particles ($\bar{r}w$: 0.08 μm)	125 parts

Comparative Example 1	
Cu-Zn-based ferrite carrier ($\bar{r}w$: 100 μm)	5,000 parts
MMA/St (25/75) ($\bar{r}w$: 0.5 μm)	75 parts

Comparative Example 2

The same composition as Example 1. Temperature was raised to 120° C.

Comparative Example 3	
Mg-Cu-Zn-based ferrite carrier ($\bar{r}w$: 44 μm)	5,000 parts
MMA resin ($\bar{r}w$: 0.4 μm)	150 parts

Comparative Example 4	
Cu-Zn-based ferrite carrier ($\bar{r}w$: 80 μm)	5,000 parts
MMA/BMA resin (8/2) ($\bar{r}w$: 0.6 μm)	100 parts

Example 1 was repeated but the material temperature was controlled to be 45° C.

The items that concern the coating carriers obtained in the above Examples and Comparative Example are shown in Table 1.

Conditions and methods of measuring properties are as follows:

1. Material temperature:

A mean value of approximate surface temperatures of particles, obtained when a temperature measuring probe is inserted in the group of particles fluidized as a result of application of an impact force so that the particles may be brought into contact with the probe at random. The temperature measuring probe is comprised of a thermocouple, a temperature measuring insulator, etc. and capable of measuring temperature by the electrical measurement of its electromotive force, resistance value, etc. The thermo couple includes, for example, a chromel-alumel thermocouple.

The material temperature in the present invention is measured by using a chromel-alumel thermocouple (manufactured by Hayashi Denko K.K.) of 10 cm in length and 6.4 mm in diameter, equipped with a cover made of stainless steel (SUS304), and inserting its end by 5 cm.

2. Method of measuring the quantity of white powder:

Into a 20 ml sample tube, 20 g of a coated carrier and 15 ml of methanol were introduced, followed by stirring for 10 minutes using a wave rotor (revolution number: 46 rpm), and the resulting supernatant was put into a cell exclusively used for a photoelectric colorimeter (wavelength: 522 nm) to measure its light transmittance. The quantity was thus determined.

3. Method of measuring $[\text{Fe}^{++}]$:

In 9 ml of an aqueous 0.001 % acetic acid solution, a solution obtained by adding 1 ml of an ethanol color identification reagent of 0.2 % 2,2-dipyridyl and a surface active agent, and 1 g of a coated carrier are introduced into a 20 ml sample bottle, followed by stirring for 2 minutes using a wave rotor (revolution number: 46 rpm). The resulting supernatant is put into a cell exclusively used for a photoelectric colorimeter (wavelength: 522 nm) to measure its light transmittance. Absorbance ($\log 1/T$) is calculated from the transmittance T thus measured, and the calculated is multiplied by a calibration factor.

$[Fe^{++}] = \log 1/T \times \text{calibration factor}$.

4. The particle diameter of the resin particles was measured using Model N-4 available from Coulter Electronics Co.

5. BET specific surface area:

Measurement was made using Micromeritics Flowsorb II, Type 2300 (manufactured by Shimadzu Corp.).

6. The rate of fusion was determined by calculation from the quantity of the coated carrier having passed through a mesh after 1.0 kg of a coated carrier was sieved using a given sieve. A sieve of 80 meshes was used for a carrier of 100 μm ; 100 meshes, for a carrier of 80 μm ; 200 meshes, for a carrier of 45 μm ; and 280 meshes, for a carrier of 25 μm .

Table 1

	Magnetic particle circularity	Resin particle size/carrier particle size	Resin particle BET surface area*	Material temperature	Resin coating time	Rate of fusion	[Fe ⁺⁺] ppm	White powder transmittance
Example:								
1	0.82	0.0008	120	70	15	≤1	0.20	98
2	0.83	0.0006	120	70	15	"	0.18	99
3	0.75	0.0006	120	70	15	"	0.18	98
4	0.80	0.0013	120	70	15	"	0.20	97
5	0.82	0.0013	65	70	20	"	0.40	97
6	0.75	0.0022	65	70	20	"	0.35	96
7	0.73	0.0024	120	70	20	"	0.40	96
8	0.82	0.0009	88	90	15	"	0.20	98
9	0.82	0.0013	67	90	20	"	0.22	97
10	0.82	0.0025	45	110	25	"	0.18	97
11	0.82	0.0010	85	90	15	"	0.20	98
Comparative Example:								
1	0.83	0.0050	15	70	*	-	-	-
2	0.82	0.0008	120	120	180	7	1.15	88
3	0.75	0.0091	20	200	180	15	1.23	83
4	0.82	0.0008	120	45	120	≤1	1.52	75

* No coated carrier was obtainable.

(Evaluation of frictional electrostatic charging performance of toner)

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Using the above respective developers, measured was the amount of frictional electrostatic charging of toners under environmental conditions of a high temperature and high humidity and under environmental conditions of a low temperature and low humidity.

However, in respect of developers comprising a combination with a carrier comprised of magnetic material particles having a weight mean particle diameter of more than 60 μm , the amount of frictional electrostatic charging of toners was measured according to a known blow-off method. In respect of developers comprising a combination with a carrier comprised of magnetic material particles having a weight mean particle diameter of not more than 60 μm , a development process was actually carried out to measure the frictional electrostatic charging performance of toners. Results obtained are shown in Table 2.

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(Actual copying test)

Using respectively the above developers of Examples 1 to 9 and Comparative Examples 2 to 4, actual copying tests to form copy images were carried out using an electrophotographic copying machine "U-Bix 5500" (manufactured by Konica Corporation) equipped with a contact type developing unit. Copying was carried out on 200,000 sheets under conditions of a high temperature and high humidity, 33 °C and 80 % RH, and under conditions of a low temperature and low humidity, 10 °C and 20 % RH. Fog and maximum density (Dmax) at the initial stage, 100,000 sheet copying and 200,000 sheet copying, respectively, were measured using SAKURA Densitometer PDA-65 (manufactured by Konica Corporation). Results obtained are shown in Table 3.

Among development conditions, however, the distance between the drum and sleeve and the distance between the doctor blade and sleeve were set to appropriate conditions depending on the particle diameter of each carrier.

Regarding the above Examples 10 and 11, the actual copying tests were also carried out to make evaluation, using an electrophotographic copying machine "U-Bix 15500" (manufactured by Konica Corporation) equipped with a contact type developing unit.

Table 2

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	Toner concentration	High temperature, high humidity 33 °C, 80 % RH	Low temperature, low humidity 10 °C, 20 % RH
Example:	%	$\mu\text{c/g}$	$\mu\text{c/g}$
1	5.0	-23	-28
2	3.5	-22	-26
3	2.5	-28	-32
4	8.0	-13	-15
5	5.0	-24	-28
6	8.0	-11	-14
7	10.0	-12	-14
8	5.0	-22	-27
9	5.0	-20	-23
10	5.0	+20	+30
11	5.0	+24	+27
Comparative Example:			
1	-	-	-
2	5.0	-16	-28
3	8.0	-6	-14
4	5.0	-14	-26

Table 3

	High temp., high humidity; 33 ° C, 80%RH						Low temp., low humidity; 10 ° C, 20%RH					
	Initial stage		100,000 copying		200,000 copying		Initial stage		100,000 copying		200,000 copying	
	Dmax	Fog	Dmax	Fog	Dmax	Fog	Dmax	Fog	Dmax	Fog	Dmax	Fog
Example:												
1	1.03	≤0.01	1.20	≤0.01	1.15	≤0.01	1.30	≤0.01	1.25	≤0.01	1.20	≤0.01
2	1.2	"	1.15	"	1.10	"	1.25	"	1.20	"	1.20	"
3	1.2	"	1.15	"	1.10	"	1.20	"	1.15	"	1.15	"
5	1.3	"	1.2	"	1.10	"	1.30	"	1.25	"	1.20	"
8	1.3	"	1.2	"	1.10	"	1.30	"	1.20	"	1.20	"
9	1.3	"	1.2	"	1.05	"	1.30	"	1.20	"	1.20	"
Comparative Example:												
2	1.3	0.01	1.00	≤0.01	0.60	0.02	1.30	0.01	1.10	≤0.01	0.90	0.01
4	1.2	0.02	0.80	0.01	0.50	0.02	1.20	0.02	1.00	0.01	0.90	0.01
Example:												
10	1.30	≤0.01	1.20	≤0.01	1.10	≤0.01	1.30	≤0.01	1.25	≤0.01	1.20	≤0.01
11	1.30	"	1.25	"	1.20	"	1.30	"	1.25	"	1.25	"
4	1.30	≤0.01	1.20	≤0.01	1.15	≤0.01	1.30	≤0.01	1.25	≤0.01	1.20	≤0.01
6	1.25	"	1.15	"	1.10	"	1.25	"	1.20	"	1.15	"
7	1.25	"	1.20	"	1.15	"	1.25	"	1.20	"	1.20	"
Comparative Example:												
3	1.30	0.01	1.00	≤0.01	0.70	0.02	1.30	0.01	1.10	≤0.01	0.80	0.01
Dmax shows the maximum density and a relative density of a developed image, assuming density at an image part of an original as 1.3. Fog shows the relative density of a developed image, assuming density at a nonimage part of an original as 0.												

As will be seen from the above results in Examples, it was possible according to Examples 1 to 11 of the present invention to obtain carriers through a simple means in a short time and yet in a high yield. In the actual copying tests, a superior durability was shown, exhibiting a stable frictional electrostatic charging performance, and the appropriate toner concentration was maintained without causing any adhesion of carrier, so that it was possible to form images with a superior development performance and a good image quality.

Because of the entire coating of the carrier surface with the resin, the carrier is free from environment dependence, possessing a uniform and tough coating, so that a stable performance can be obtained under conditions including a high temperature and high humidity and a low temperature and low humidity.

The coated carrier can also be prepared in a short time. Even when the coverage is changed, only the mixing ratio may be changed, where the coating time is not prolonged.

Claims

1. A carrier for an electrostatic image development comprising magnetic material particles covered with resin particles, wherein said carrier is prepared by applying a repeated impact force at a material

temperature within the range of from 50 to 110 °C to a mixture of magnetic material particles having a weight mean particle diameter of from 10 to 200 μm and resin particles having a weight mean particle diameter of less than 1/200 of that of the magnetic material particles.

2. The carrier of claim 1, wherein said weight mean particle diameter of said resin particle is within the range of from 1/2000 to less than 1/200 of that of the magnetic material particles.

3. The carrier of claim 1, wherein the circularity of said magnetic material particles is not less than 0.7.

4. The carrier of claim 1, wherein BET specific surface area of said resin particles is from 40 m²/g to 6000 m²/g.

5. The carrier of claim 1, wherein the circularity of said magnetic material particles is not less than 0.7 and BET specific surface area of said resin particles is from 40 m²/g to 6000 m²/g.

6. The carrier of claim 1, wherein the mixing ratio of said magnetic material particles to said resin particles is 100 to 0.1~10 by weight.

7. The carrier of claim 1, wherein the mixing ratio of said magnetic material particles to said resin particles is 100 to 0.5~4 by weight.

8. A method of manufacturing a carrier for an electrostatic image development comprising magnetic material particles covered with resin particles by applying a repeated impact force at a material temperature within the range of from 50 to 110 °C to a mixture of magnetic material particles having a weight mean particle diameter of from 10 to 200 μm and resin particles having a weight mean particle diameter of less than 1/200 of that of the magnetic material particles.

9. The method of manufacturing said carrier of claim 8, wherein said weight mean particle diameter of said resin particle is within the range of from 1/2000 to less than 1/200 of that of the magnetic material particles.

10. The method of manufacturing said carrier of claim 8, wherein the circularity of said magnetic material particles is not less than 0.7.

11. The method of manufacturing said carrier of claim 8 by applying a repeated impact force at a material temperature within the range of from 50 to 110 °C for 10 to 60 minutes to said mixture.

12. The method of manufacturing said carrier of claim 8, wherein BET specific surface area of said resin particles is from 40 m²/g to 6000 m²/g.