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(54) **Method for making magnetic toner.**

(57) A method for making a magnetic toner which comprises agitating magnetic matrix particles in a high speed mixer until the particles are heated to a temperature between the melting point and the softening point of binder contained in the matrix particles. To the heated matrix particles are immediately added conductive particles, followed by agitating at high speed thereby depositing conductive particles on the surface of the individual matrix particles. The surface of the matrix particles becomes softened, so that the conductive particles are deposited to form a uniform, tenacious coating on the matrix particle surface. These coated particles are classified to have a desired size.

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TITLE

METHOD FOR MAKING MAGNETIC TONER

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to electrostatic recording and more particularly, to a method for making magnetic toners for electrostatic development in electrophotography, electrostatograpy, electrostatic printing and the like.

Description of the Prior Art

Magnetic toners are usually composed of binder resins, magnetic materials, resistance-adjusting agents and optionally colorants and fluidizing agents. These magnetic toners have the advantage that no control in concentration of magnetic toner is required because no carrier is contained and use of the toner allows a simpler construction or mechanism of developing device. In order to suitably control the resistance of magnetic toner, it is necessary to disperse conductive particles such as of carbon black in individual magnetic toner particles or to form a conductive layer on the surface of individual particles. The control is easier in the latter case.

Typical methods of forming a conductive layer include:

a) Mixing conductive particles and magnetic toner matrix particles together in a stream of hot air such as in fluidized drying furnace thereby depositing the conductive particles on the surface of each matrix particle to form a conductive layer thereon; and

b) Mixing conductive particles and magnetic matrix particles in a rotary drum to form a conductive layer on each matrix particle.

However, these methods have several drawbacks that mere mixing of magnetic toner matrix particles and conductive particles will not permit sufficient deposition of the conductive particles on the matrix particles, it being thus difficult to form a stable, uniform conductive layer on each matrix particle, that the amount of treatment per unit hour is relatively small, and that it is rather difficult to obtain a magnetic toner of constant resistance. The application of the magnetic toners produced by these methods results in low image density and frequent occurrence of fogging, leading to the lowering of image quality.

The above defect is emphasized especially in magnetic roll developments using insulating magnetic rolls such as, for example, an anodized aluminium sleeve, a plastic resin sleeve and the like.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a method for making a magnetic toner which overcomes the drawbacks of the prior art techniques and in which the toner of stable quality can readily be prepared in large quantities.

It is another object of the invention to provide a method for making a magnetic toner exhibiting low resistivity and good flowability whereby the toner ensures much reduced occurrence of fogging phenomenon and very excellent image quality and density even when applied in an insulating magnetic roll developing system.

It is a further object of the invention to provide a method for making a magnetic toner in which conductive particles uniformly deposited on and dispersed in the surface of individual magnetic matrix particles which have been softened but not molten thereby forming a uniform tanacious coating on each particle of the matrix.

It is a still further object of the invention to provide a magnetic toner which can give excellent results when used to develop in any known magnetic roll developing systems utilizing rotation of sleeve, rotation of magnet and simultaneous rotation of both magnet and sleeve.

The above objects can be achieved according to the present invention by a method which comprises agitating magnetic matrix particles, each comprising at least a binder material and a magnetic material, in a high speed mixer until the particles are frictionally heated to a temperature between the melting point and the softening point of the binder material, adding a predetermined amount of conductive particles to the heated matrix particles, further agitating the mixture to permit the conductive particles to deposit on the surface of the individual matrix particles as a tenacious coating, and classifying the resulting particles to have a predetermined range of size. In the high speed mixer, the matrix particles are agitated and heated by means of an agitator fitted with a rotor. The peripheral speed of the rotor should preferably be in the range of from 200 m/min to 2000 m/min in order to realize the intended level of the temperature.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a perspective schematic view of a cell for measuring the resistivity of magnetic toner; and

Fig. 2 is a perspective schemativ view of an instrument for measuring the flowability of magnetic toner.

PREFERRED EMBODIMENT OF THE INVENTION

According to the method of the invention, magnetic toner particles are first agitated and mixed together in any known types of high speed mixer having an agitator until they are heated to a temperature between the melting point and the softening point of a binder material contained in the matrix particles. The actual temperature level to which the matrix particles must be heated depends on the binder material used but is generally in the range of approximately 30 - 80°C, preferably 40 - 60°C and most preferably 45 - 50°C, at which an ordinary binder resin or material used for this purpose, e.g. an epoxy resin, a styrene resin, polyethylene wax or the like, can be softened. The reason why the particles are heated during the mixing is due to the fact that when agitated at high speed, high shearing force of the agitator is exerted on the particles, so that heat generates by fricational force among the particles and between the particles and the rotor of agitator and wall surfaces of the mixer. The high speed mixer is, for example, Super Mixer made by Kawada Mfg Co., Ltd., Henchel Mixer made by Mitsui-Miike Mfg. Co., Ltd., or the like. As a matter of course, any mixers which can yield such a high shearing force as mentioned above may be used in the practice of the invention. The agitation is carried out under conditions of vigorous agitation with an agitator fitted with a rotor whose peripheral speed is in the range of from 200 m/min to 2000 m/min whereby the generation of heat becomes sufficient to attain a desired level of temperature. Smaller peripheral speeds may not cause the matrix particles to be softened, which makes is difficult to firmly deposit on the matrix particles conductive particles of smaller sizes than the matrix particles. On the other hand, larger peripheral speeds show the tendency that among conductive particles which have once deposited on the matrix particles, the particles of smaller sizes than the matrix particles are liable to fall off and thus a uniform coarting cannot be obtained. It will be noted that prior to the agitation, the matrix particles may be classified by a suitable means to improve a yield of final product. In this case, the size of the particles is generally in the range of from 5 to 60 microns, preferably 10 to 44 microns.

To the thus heated matrix particles are immediately added conductive particles serving as a resistance adjuster, followed by high speed mixing or agitation under the same agitating conditions as in the first agitation to uniformly disperse the both particles. As a result, the conductive particles adhere to and deposit on the individual softened matrix particles to form a tenacious coating of the conductive particles on the surface of each matrix psarticle. The conductive particles are usually added in an amount ranging from 1 to 5 wt% of the matrix particles charge. The amount is varied, within the above-defined range, depending on an intended resistivity level of the final magnetic toner product.

The conductive particles are made of any of conductive materials, and carbon black is used for general purpose because of its availability and inexpensiveness.

Aside from the resistance adjuster, any known additives such as charge-controlling particles may be added together with the resistance adjuster after heating of the matrix particles.

The magnetic toner thus obtained in accordance with the method of the present invention are classified to have a predetermined size of from 5 to 60 microns, preferably 10 to 44 microns. This magnetic toner can give good results when fixed on recording paper by any known fixing systems including 1) fixing by heating, 2) fixing by application of pressure, and 3) fixing by application of heat and pressure in combination.

The present invention is described in more detail by way of examples and comparative examples.

[Example 1]

A starting material for toner composed of 50 parts by weight of an epoxy resin (Epikote No. 1004, by Shell Chem. Co.), and 50 parts by weight of iron oxide (Magnetite EPT-500, by Toda Ind. Co., Ltd.) was kneaded in a biaxial kneader and reduced into particles with a size below 2 mm by means of the Rotoplex powdering machine (Itoman Engineering Model 8/16), followed by finely powdering in a pin mill (Alpine : 160 z). The resulting powder was classified by means of a wind power classifier (Alpine 100 MZR) to have a size ranging from 10 to 44 microns, and then agitated in a high speed agitated mixer (Super Mixer SMG-20, by Kawada Mfg. Co.) until it was self-heated up to 45°C. Immediately, carbon black to be the resistance adjuster (Carbon Black #44, by Mitsubishi Chem. Co., Ltd.) was added in an amount of 3 wt% of the magnetic matrix particles, followed by agitating at 1900 r.p.m. for 30 seconds thereby coating or depositing the conductive particles on the surface of the individual matrix particles in a uniform and tenacious manner (which treatment is hereinafter referred to as surface coating). The resulting particles were again subjected to the wind power classifier to have a size of from 10 to 44 microns.

This magnetic toner was placed in a cell shown in Fig. 1 to measure its resistivity. The resistivity was found to be 2.00×10^3 ohms-cm. In Fig. 1, indicated at 1 are copper electrodes each having a length of 1 cm, a width of 1 cm and a thickness of 0.03 cm, the electrodes being spaced from each other at a distance of 1 cm, at 2 is a glass cell having an inner wall dimension of 1 cm in length, 1.06 cm in width and 3 cm in height, and at 3 are covered wires each connected to the electrode at one end and also to one of terminals of the Wheatstone bridge at the other end. The magnetic toner is charged into the cell to a certain level for the measurement.

The magnetic toner was then subjected to the measurement of flowability using an instrument shown in Fig. 2, which includes a brass plate 4 having a thickness of 0.15 cm and formed with through-holes 7 of different sizes indicated in the figure, a ring 5 having an inner diameter of

0.8 cm and a height of 1 cm, and a frame 6 supporting the plate 4. In measuring operation, the ring 5 is placed just on an arbitrary through-hole and a magnetic toner to be measured is charged into the ring 5. The flowability is represented by a diameter of the smallest through-hole 7 through which the charged toner starts to drop. The magnetic toner obtained in this example showed a flowability of 0.6 mm.

Further, the magnetic toner particles were subjected to the measurement of angle of repose by a powder tester (Model PT-E, by Hosokawa Micron Co., Ltd.). The angle of repose which is a measure for flowability was found to be 31°.

The magnetic toner was used to develop by the magnetic roll developing techniques in which magnets were rotated with respect to aluminium and insulating sleeves and then thermally fixed thereby obtaining high quality visible images of high density which were completely free of any fogging. Similar excellent results were also obtained by other magnetic roll developing systems including the sleeve rotation system and the sleeve and magnet simultaneous rotation system.

To confirm the reproducibility, the procedure of Example 1 was exactly repeated five times. The values of resistivity, flowability and angle of repose are shown in

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Table 1, revealing that good reproducibility is obtained. The results of the development and fixation were also excellent similar for Example 1.

Table 1

Test No. / Characteristics	1	2	3	4	5
Resistivity (x 10^3 ohms-cm)	2.01	2.08	1.92	2.04	1.95
Flowability (mm)	0.6	0.6	0.5	0.6	0.6
Angle of repose (degree)	31	31	31	31	31

[Comparative Example 1]

600 cc of the magnetic matrix particles obtained in Examle 1 were charged into a 1 liter wide mouth bottle, to which was added the resistance adjuster in an amount of 2 wt% based on the matrix particles, followed by the surface coating treatment on a shaker for 30 minutes. The resulting magnetic toner was subjected to the wind power classifier to have a size of 10 - 44 microns. The magnetic toner had a resistivity of 8 x 10^4 ohms-cm, a flowability of 0.9 mm, and an angle of repose of 34 degrees when measured in the same manner as in Example 1.

Similarly, 2.5 liters of the magnetic matrix particles obtained in Example 1 was charged into a 5 liters ball mill pot, to which was added the carbon black resistance adjuster in an amount of 2 wt% based on the matrix particles. The matrix particles were surface coated by shaking for 3 hours and then classified by means of the wind power classifier to have a size of from 10 to 44 microns. The thus classified magnetic toner had a resistivity of 2×10^5 ohms-cm, a flowability of 1.2 mm and an angle of repose of 35 degrees on measurement in the same manner as in Example 1.

The both magnetic toners were applied as usual and developed by magnetic roll developing techniques and thermally fixed, with the result that there could be obtained in both cases high quality visible images of high density which were free of any fogging when developed using an conductive aluminium sleeve. However, the development using an insulating magnetic roll resulted in generation of fogging phenomenon with the image being low in density and having a reduced commercial value.

Then, the reproducibility test was conducted repeating, five times, the respective procedures of Comparative Example 1 using the shaker and the ball pot mill. The resistivities, flowabilities and angles of repose of the resulting magnetic toners were so fluctuated as shown in Tables 2 and 3.

Table 2

Processing with Shaker

Characteristics \ Test No.	1	2	3	4	5
Resistivity (x 10^3 ohms-cm)	10	15	62	43	27
Flowability (mm)	0.9	0.9	1.1	1.1	1.0
Angle of repose (degree)	34	35	36	35	35

Table 3

Processing with Ball Mil

Characteristics \ Test No.	1	2	3	4	5
Resistivity (x 10^3 ohms-cm)	300	250	90	640	150
Flowability (mm)	1.2	1.2	1.2	1.3	1.1
Angle of repose (degree)	36	35	35	36	34

[Example 2]

Example 1 was repeated using a starting material for toner composed of 40 parts by weight of a styrene resin

(Picolastic D-125, Esso), 10 parts by weight of low molecular weight polypropylene (Biscall 550P, by Sanyo Chem. Co., Ltd) and 50 parts by weight of iron oxide (Magnetite EPT 500, by Toda Ind. Co., Ltd.), thereby obtaining a magnetic toner.

The characteristics of this magnetic toner were measured in the same manner as in Example 1. As a result, it had a resistivity of 1.5 x 10^3 ohms-cm, a flowability of 0.5 mm, and an angle of repose of 30 degrees.

The magnetic toner was used for development by magnetic roll developing techniques and fixed by a heat roll. In both developing systems using conductive and insulating rolls, there were obtained high quality visible images of high density free of any fogging involved.

[Comparative Example 2]

The procedure of Comparative Example 1 was repeated using the magnetic toner matrix particles obtained in Example 2. The resulting magnetic toner was subjected to the measurement of its characteristics in the same manner as in Example 1 and found to have a resistivity of 9 x 10^4 ohms-cm, a flowability of 1.0 mm and an angle of repose of 35 degrees.

Further, 2.5 liters of the magnetic toner matrix particles obtained in Example 2 were charged into a 5 liters ball mill pot, to which was added the carbon black resistance adjuster in an amount of 2 wt% based on the matrix particles, followed by surface coating of the matrix particles with the carbon black for 3 hours. The resulting magnetic toner was classified by a wind power classifier to have a size of from 10 to 44 microns. When measured in the same manner as in Example 1, the magnetic toner had a resistivity of 1.5×10^5 ohms-cm, a flowability of 1.2 mm, and an angle of repose of 35 degrees. The magnetic toner was used for development by magnetic roll developing techniques and fixed with a heat roll. Although a high quality visible image of high density which was free of any fogging was obtained by the developing method using the conductive aluminium sleeve, the image obtained using the insulating magnetic roll suffered fogging with its density being low, and had thus little commercial value.

[Example 3]

Example 1 was repeated using a starting material for toner composed of 30 parts by weight of polyethylene wax (Hi-wax 200P, Mitsui Petroleum Chem. Co., Ltd.), 10 parts by weight of EVA (Evaflex #260, by Mitsui Polychemical Co., Ltd.) and 60 parts by weight of iron oxide (Magnetite EPT-500, by Toda Ind. Co., Ltd.).

The resulting magnetic toner was subjected to the measurement of characteristics, revealing that it had a resistivity of 1.8×10^3 ohms-cm, a flowability of 0.6 mm and an angle of repose of 31 degrees.

The magnetic toner was used for development by mangetic roll techniques and fixed by a press fixing roll thereby obtaining high quality visible images of high density free of any fogging in both the conductive and insulating roll developing systems.

[Comparative Example 3]

The magnetic tonner matrix particles obtained in Example 3 were used and treated in the same manner as in Comparative Example 1 using a shaker and a ball mill to obtain two types of magnetic toner. The magnetic toner treated by the shaker had a resistivity of 7×10^4 ohms-cm, a flowability of 1.1 mm and an angle of repose of 35 degrees and the magnetic toner obtained in the ball mill had a resistivity of 5×10^5 ohms-cm, a flowability of 1.2 mm and an angle of repose of 35 degrees.

The both magnetic toners were used for development by magnetic roll developing techniques and fixed by a press fixing roll. Although high quality visible images of high density which were completely free of any fogging were obtained by the developing method using the conductive aluminium sleeve, the images obtaind by the insulating magnetic roll suffered fogging with their density being low, and had thus little commercial value.

It should be noted that appropriate binder materials, magnetic materials and resistance adjusting material other than those set forth in these examples can be used as long as they are ordinarily used for this purpose. These will not be set forth since they are well known.

CLAIMS

1. A method for making a magnetic toner comprising agitating magnetic matrix particles, each comprising at least a binder material and a magnetic material, in a high speed mixer until the particles are frictionally heated to a temperature between the melting point and the softening point of the binder material, adding a predetermined amount of conductive particles to the heated matrix particles, further agitating the mixture to deposit a tenacious coating of the conductive particles on the surface of the individual matrix particles, and classifying the resulting particles to have a predetermined range of size.

2. A method according to Claim 1, wherein the matrix particles are mixed in the presence of an agitator fitted with a rotor whose peripheral speed is in the range of from 200 m/min to 2000 m/min.

3. A method according to Claim 1 or 2, wherein said conductive particles are added in an amount of from 1 to 5 wt% based on the charged matrix particles.

4. A method according to any one of the preceding claims, wherein said resulting particles have a size of from 5 to 60 microns.

5. A method according to any one of the preceding claims, wherein prior to agitating of the matrix particles, the matrix particles are classified to have a predetermined range of size.

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FIG. 1

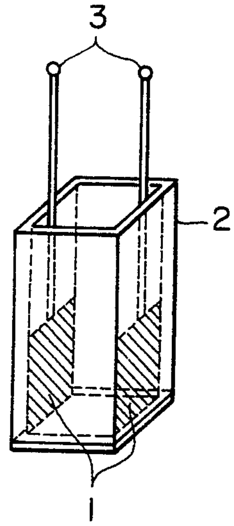
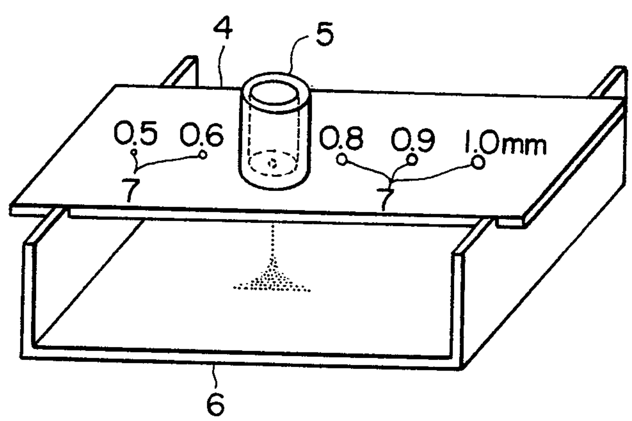


FIG. 2



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Application number

European Patent Office

EUROPEAN SEARCH REPORT

EP 82300538.4

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
A	US - A - 4 199 614 (ZIOLO) --	1
A	GB - A - 1 548 242 (SUBLISTATIC) ----	1

CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)

G 03 G 9/08

TECHNICAL FIELDS SEARCHED (Int.Cl. 3)

G 03 G

C 09 C

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same category
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: earlier patent document, but published on, or after the filing date
D: document cited in the application
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&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	14-05-1982	SALTEN

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