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(54) **Dry electrostatographic developer composition and method for developing electrostatic latent images.**

(57) In the development of an electrostatic latent image by means of a dry electrostatographic developer composition, a developed image of low granularity is obtained by the use of a developer having a ferrite carrier of small particle size, a toner of small particle size and by maintaining a low concentration, e.g., less than 12 weight percent, of toner in the developer.

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This invention relates to dry electrostatographic developer compositions and, more particularly to a composition comprising ferrite carrier particles and thermoplastic toner particles, which composition is used in the method of the invention to form toner images having low granularity.

Various processes are known, such as electrophotography and dielectric recording, for recording images by development of an electrostatic charge latent image. They have in common the fact that an electrostatic charge pattern is formed on an insulating surface and is developed, i.e., made visible, by contact with a developer composition containing charged toner particles. These are attracted to the oppositely charged latent image where they can be fixed or transferred to another surface to which they are fixed.

Two kinds of developer compositions are in use for developing electrostatic charge latent images -liquid developers and dry developers. Liquid developers are dispersions of colloidal toner particles in a volatile insulating dispersing liquid such as a low-boiling hydrocarbon liquid. Dry developers are mixtures of relatively large magnetic carrier particles and powdered thermoplastic toner particles, the latter usually being colored to make the developed image visible.

Of these two kinds of developers, liquid developers have been preferred when a developed image having high resolution and low granularity is required, as in high quality reproduction of continuous tone photographic images and in development of microimages. They have been preferred because of the fine particle size of the colloidal particles. Dry developers have been less desirable for such uses because of larger particle size and a tendency toward clumping or agglomeration of the dry toner particles. A drawback, however, in the use of liquid developers is the fact that the solvent must be vaporized to fix the image. This poses environmental and safety problems.

A continuing problem in the dry development of electrostatic latent images, especially gray-scale or continuous-tone images, is granularity and poor resolution. "Gray-scale" images are images formed, for example, in the reproduction of photographs which have gray tones which vary in optical density. In this usage, gray means a density intermediate between the maximum and minimum densities possible, whether colored or neutral; in such gray areas, graininess is most noticeable and objectionable. Because they have in the past formed grainy gray-scale images, dry developers consisting of a mixture of carrier particles and powdered toner have not been considered to be as suitable as liquid developers for producing images of high resolution and low granularity.

A need exists, therefore, for a dry developer which requires no solvent, which can be thermally fixed and which produces images of low granularity.

In accordance with the present invention, a dry electrostatographic developer composition is provided which is capable of developing images with very low granularity and high resolution. The composition of the invention comprises:

(a) ferrite carrier particles having an average particle size of from 5 to 50 μm, and

(b) thermoplastic toner particles having an average particle size less than 12 μm,

the concentration of toner particles in the developer composition being below 12 weight percent.

In the method of the invention, such a composition is used to form an image of low granularity.

The two basic components of the developer compositions of the invention are the carrier particles and the toner particles. The carrier particles are hard magnetic ferrite particles such as disclosed in the patent to Miskinis et al, U.S. 4,546,060. Such ferrites are magnetic oxide compounds containing iron as the major metallic component. For example, they are compounds of ferric oxide, Fe_2O_3, with basic metallic oxides, $MFeO_2$ or MFe_2O_4, where M is a mono- or divalent metal and iron is in the oxidation state of +3. Ferrites also include compounds of barium or strontium such as $BaFe_{12}O_{19}$, $SrFe_{12}O_{19}$ and magnetic compounds of the formula, $MO \cdot 6Fe_2O_3$, where M is barium, strontium or lead, as disclosed in the patent to Shirt, U.S. 3,716,630. Strontium and barium ferrites are the preferred carrier particle materials.

The ferrite carrier particles in the developer compositions of the invention are of smaller particle size than many known carrier particles. They are, however, larger than the toner particles. An average carrier particle size in the range from 5 to 50 μm is useful, and the preferred range is 15 to 40 μm.

To improve triboelectric charging of the toner particles in the developer composition, the carrier particles are usually coated with a resin having the appropriate triboelectric relationship to the binder resin of the toner particles. Examples of useful resin coatings include those described in the patent to McCabe, U.S. 3,795,617; and the patents to Kasper U.S. 3,795,618 and 4,076,857. For use with toners which are to be positively charged, preferred resins for the ferrite carrier coating include fluorocarbon polymers such as poly-(tetrafluoroethylene), poly(vinylidene fluoride) and poly(vinylidene fluoride-co-tetrafluoroethylene).

The toner component of the developer composition of the invention is a powdered thermoplastic resin which, preferably, is colored. It can be prepared by melt compounding a resin with a col-

orant, i.e., a pigment or a dye, and any other desired addenda, of which a charge control agent is usually desired.

Examples of useful thermoplastic toner resins or polymers are disclosed, for example in the patent to Kasper et al, U.S. 4,076,857. Especially useful are crosslinked polymers disclosed in the patent to Jadwin et al, U.S. 3,938,922 and the patent to Sadamatsu et al, U.S. 3,941,898. Copolymers of styrene or lower alkyl styrenes with acrylic monomers such as lower alkyl acrylates and methacrylates are particularly useful. Preferably, they are lightly crosslinked with divinyl benzene. Also preferred are various condensation polymers, especially polyesters and copolyesters.

The shape of toner particles can be irregular, as in the case of ground toners, or spherical. The latter can be obtained by spray drying a solution of the toner resin in a solvent or by the polymer synthesis procedure, known as limited coalescence suspension polymerization. The latter is described, for example, in U.S. Patent No. 3,615,972.

To prepare the developer compositions of the invention, the carrier particles and toner particles are first subjected to any necessary classification procedure to obtain particles of the desired average particle size range. The carrier particle size range has already been mentioned. By employing such small carrier particles, one consequence is that formation of scratches or so-called rake lines in the developed image is avoided or reduced. These can appear in large toned areas of the image when developed by the magnetic brush method with a developer containing large coarse carrier particles.

As for the toner particles, they are of small size in the developer compositions of the invention. The average particle size is below 12 μm and preferably is in the range from 1 to 12 μm and most preferably in the range from 1 to 6 μm. A fraction of particles of this desired range can be recovered from a mixture with larger toner particles by air classification.

An unexpected result observed in accordance with the present invention is that when a developer composition containing such small carrier and toner particles is employed for image development, the granularity of the developed image is remarkably low when the toner concentration in the developer composition is maintained at a low level. More specifically, by maintaining the toner concentration (Tc) of such developer at below 12 weight percent (based on the total developer weight) and, preferably, in the range from 3 to 8 weight percent, unexpected reduction in the granularity of the developed image is achieved.

The preferred method of applying the developer to the electrostatic latent image is disclosed by Miskinis et al., U.S. Patent No. 4,546,060. Briefly, the method employs a magnetic brush assembly consisting of an array of permanent magnets rotating within a concentric, non-ferromagnetic, rotatable, electrically conducting shell. The above developer, when applied to the shell, is caused to flow vigorously in a tumbling motion over the closely-spaced latent image, thereby rendering it visible. The following examples more fully illustrate the practice of the present invention. Percentages and parts are by weight.

EXAMPLE 1

A developer was prepared at a toner concentration of 4% by mixing together 4 parts of toner and 96 parts of carrier. The toner consisted of a 6 μm fraction (volume-average) of "fines" separated by a gas classifier from a commercially available toner powder which comprised styrene/butyl acrylate copolymer crosslinked with divinyl benzene and containing carbon black ("Regal 300"™ of Cabot Corp.) as a colorant and benzyloctadecyldimethylammonium 3-nitrobenzenesulfonate as a charge control agent.

The carrier particles were permanently magnetized and comprised a strontium ferrite core having a thin coating of poly(vinylidene fluoride) resin ("Kynar"™ resin of Pennwalt Corp.).

The charge-to-mass ratio (Q/m) of the developer was found to be 237.1 microcoulombs/g as measured by the ESCA method (i.e., by vibrationally separating the toner from the carrier in an electric field and then measuring the toner's charge and mass).

The developer was applied to a homogeneous-type single use organic photoconductor (SO-102™ photoconductor available from Eastman Kodak Company), whose surface had been charged to a potential of 550 volts, with a magnetic brush biased at a potential of 495 volts. The brush comprised a 4.45 cm-diameter array of permanent magnets rotating at 2000 RPM inside an aluminum shell rotating at 100 RPM. Photoconductor-to-shell spacing was 0.38 mm. The photoconductor was moved at 5.1 cm/sec relative to the brush. Brush bias was adjusted in this and the next three examples to maintain a resultant toner image optical density of about 0.95.

The resulting deposit of toner was smooth and free from noticeable graininess, For comparison with the graininess of other examples, the deposit was scanned with the long narrow slot of an optical scanning apparatus to obtain a Wiener spectrum. See T.H. James, "The Theory of the Photographic Process", 4th Edit, 1977, MacMillan Publishers. This produced a visually-weighted noise power of σ_{visual} = 53, which quantitatively indicates low

granulanity.

EXAMPLE 2

The procedure and materials were the same as in Example 1, but the toner concentration was 8%. Q/m was 126 and development bias was 240 volts. The resulting toner deposit was smooth and free from noticeable graininess. σ_{visual} was found to be about 56.

CONTROL EXAMPLE A

The procedure and materials were the same as in Example 1, but the toner concentration was 12%. Q/m was 81 and development bias was 150 volts. The resulting toner deposit was less smooth and more grainy than the above. σ_{visual} was found to be 63.

CONTROL EXAMPLE B

The procedure and materials were the same as in Example 1, but the toner concentration was 20%. Q/m was 32.3 and development bias was 100 volts. The resulting toner deposit was less smooth and more grainy than those of Examples 1 and 2. σ_{visual} was found to be 80.

In summary, Example 1 with a toner concentration of 4% shows a 34% improvement in σ_{visual} over that of Control Example B, where the toner concentration was 20%.

While neither the toner particles nor the carrier particles in the above examples possess the minimum surface areas exhibited by perfect spheres, it has been found useful to treat them as such in a calculation directed toward estimating the percentage of carrier surface that is covered by toner particles at various concentrations. When this is done, it has been found that optimum development (with respect to image quality, graininess, and resolution) occurs when from 15 to 50% of the carrier's surface area is covered by a monolayer of toner. Furthermore, this appears to hold for other methods of development, e.g., for conventional magnetic brush development with stationary magnets, carrier particle sizes as large as 130 μm, and toner particles of 13 μm.

Claims

1. An electrostatographic developer composition for producing toner images of high resolution, which comprises:
(a) ferrite carrier particles and
(b) thermoplastic toner particles,
characterized in that: the carrier particles have an average particle size of from 5 to 50 μm; the toner particles have an average particle size less than 6 μm; and the concentration of toner particles in the developer composition is below 12 weight percent.

2. A developer composition according to Claim 1 wherein the carrier particles have an average particle size of from 15 to 40 μm and the concentration of toner particles is from 3 to 8 weight percent.

3. A method of forming a toner-developed electrostatic image of low granularity which comprises:
developing an electrostatic latent image by magnetic brush contact with a developer composition comprising ferrite carrier particles and thermoplastic toner particles, characterized in that:
the toner particles have an average particle size less than 6 μm; and the concentration of toner particles in the developer composition is sufficient to provide a monolayer of toner particles covering 15 to 50 percent of the surface area of the carrier particles.

4. A method of reducing granularity in a toner image characterized by the steps of:
(a) developing an electrostatic latent image with a developer composition comprising
ferrite carrier particles having an average particle size of from 5 to 50 μm, and
thermoplastic toner particles of average particle size less than 6 μm; and
(b) replenishing toner in the developer composition to maintain a toner concentration below 12 weight percent and sufficient to maintain a monolayer of toner on the carrier particles covering 15 to 50 % of the surface area of the carrier particles.

5. The method according to Claim 4 wherein the toner concentration is maintained in the range from 3 to 8 weight percent.

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EUROPEAN SEARCH REPORT

Application Number

EP 92 11 0141

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	US-A-4 996 126 (MASAHIRO ANNO, EIICHI SANO) * column 6, line 51 * * column 11, line 33 - line 35; claim 1 * ---	1-5	G03G9/08 G03G9/10
A	US-A-4 837 101 (ROBERT J. GRUBER ET AL.) * column 6, line 19 - line 27; claim 1 * ---	1-5	
A	JAPANESE PATENTS ABSTRACTS Week 8847, Derwent Publications Ltd., London, GB; AN 88-335805 (47) & JP-A-63 250 662 (RICOH K.K.) 18 October 1988 * abstract * -----	1-5	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G03G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	11 SEPTEMBER 1992	HINDIAS E.

CATEGORY OF CITED DOCUMENTS

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