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EUROPEAN PATENT APPLICATION

21 Application number : **92308236.6**

51 Int. Cl.⁵ : **G03G 9/087, G03G 9/097**

22 Date of filing : **10.09.92**

30 Priority : **10.09.91 US 757106**

43 Date of publication of application :
17.03.93 Bulletin 93/11

64 Designated Contracting States :
DE FR GB

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54 **Developer compositions.**

57 A developer composition comprised of a toner comprised of resin, carbon black, magnetite, and a positive charge enhancing additive, and a surface additive mixture comprised of a polymeric hydroxy compound and a colloidal silica treated with a quaternary ammonium salt compound; and carrier particles comprised of a ferrite core with a polymer mixture coating thereover.

The present invention is generally directed to toners, developers, and imaging processes, including full color processes for forming multiple color images, and more specifically, the present invention is directed to developer compositions with surface additives.

United States patents Nos. 4,288,517; 4,301,228; 4,533,616; 4,828,954; and 4,973,540 disclose toner and developer compositions.

Toner compositions with colored pigments are known. For example, there are illustrated in U.S. Patent 4,948,686 processes for the formation of two-color images with a colored developer comprised of a first toner comprised of certain resin particles, such as styrene butadiene, a first pigment such as copper phthalocyanine, a charge control additive, colloidal silica and metal salts of fatty acid as external surface additives, and a first carrier comprised of a steel core with, for example, a terpolymer overcoating; and a second developer comprised of a black toner, a second charge additive and a steel core carrier with certain polymeric overcoatings. Examples of colored toner pigments are illustrated in column 9, lines 10 to 26, and examples of charge additives for the toner are detailed in column 9, lines 27 to 43, of the aforementioned patent. For the black toner, there can be selected the components as recited in columns 10 and 11, including charge additives such as distearyl dimethyl ammonium methyl sulfate, see column 11, lines 16 to 32. Additionally, the working Examples of this patent detail the preparation of a number of specific toners. Also, there is illustrated in the 4,948,686 patent a process for forming two-color images which comprises, for example, (1) charging an imaging member in an imaging apparatus; (2) creating on the member a latent image comprising areas of high, intermediate, and low potential; (3) developing the low areas of potential by conductive magnetic brush development with a developer comprising a colored first toner comprising a first resin present in an amount of from about 80 to about 98.8 percent by weight and selected from the group consisting of polyesters, styrene-butadiene polymers, styreneacrylate polymers, styrene-methacrylate polymers, and mixtures thereof; a first pigment present in an amount of from about 1 to about 15 percent by weight and selected from the group consisting of copper phthalocyanine pigments, quinacridone pigments, azo pigments, rhodamine pigments, and mixtures thereof; a charge control agent present in an amount of from about 0.2 to about 5 percent by weight; colloidal silica surface external additives present in an amount of from about 0.1 to about 2 percent by weight; and external additives comprising metal salts or metal salts of fatty acids present in an amount of from about 0.1 to about 2 percent by weight; and a first carrier comprising a steel core with an average diameter of from about 25 to about 215 microns and a coating selected from the group consisting of methyl terpolymer, polymethyl

methacrylate, and a blend of from about 35 to about 65 percent by weight of polymethyl methacrylate and from about 35 to about 65 percent by weight of chlorotrifluoroethylene-vinyl chloride copolymer, wherein the coating contains from 0 to about 40 percent by weight of the coating of conductive particles and wherein the coating weight is from about 0.2 to about 3 percent by weight of the carrier; (4) subsequently developing the high areas of potential by conductive magnetic brush development with a developer comprising a black second toner comprising a second resin present in an amount of from about 80 to about 98.8 percent by weight and selected from the group consisting of polyesters, styrene-butadiene polymers, styrene-acrylate polymers, styrene-methacrylate polymers, and mixtures thereof; a second pigment present in an amount of from about 1 to about 15 percent by weight; and a second charge control additive present in an amount of from about 0.1 to about 6 percent by weight; and a second carrier comprising a steel core with an average diameter of from about 25 to about 215 microns and a coating selected from the group consisting of chlorotrifluoroethylene-vinyl chloride copolymer containing from 0 to about 40 percent by weight of conductive particles at a coating weight of from about 0.4 to about 1.5 percent by weight of the carrier; polyvinylfluoride at a coating weight of from about 0.01 to about 0.2 percent by weight of the carrier; and polyvinylchloride at a coating weight of from about 0.01 to about 0.2 percent by weight of the carrier; and (5) transferring the developed two-color image to a substrate. Imaging members suitable for use with the process of the copending application may be of any type capable of maintaining three distinct levels of potential. Generally, various dielectric or photoconductive insulating materials suitable for use in xerographic, ionographic, or other electrophotographic processes may be selected for the above process. Examples of suitable photoreceptor materials include amorphous silicon, layered organic materials as disclosed in U.S. Patent 4,265,990 and the like. The aforementioned colored toners may be selected for utilization with the black toner and developer of the present invention in embodiments.

Processes for obtaining electrophotographic, including xerographic, and two-colored images are known. In U.S. Patent 4,264,185 there is illustrated an apparatus for forming two-color images by forming a bipolar electrostatic image of a two-color original document on a photoconductive drum. A first developing unit applies a toner of a first color and polarity to the drum and a second developing unit applies a toner of a second color and polarity to the drum to form a two-color electrostatic image which is transferred and fixed to a copy sheet. A bias voltage of the first polarity is applied to the second developing unit to repel the toner of the first color and prevent degra-

dition of the first color toner image. A bias voltage of the second polarity is applied to the first developing unit to prevent contamination of the first color toner with the second color toner. A similar full color process can be selected for the present invention in embodiments and wherein, for example, there are developed four images, one with the black toner of the present invention, and the others with three different colored toners.

Also, the following United States patents are mentioned: 4,308,821 wherein there is disclosed a method and apparatus for forming two-color images which employs two magnetic brushes; 4,378,415, which discloses a method of highlight color imaging which comprises providing a layered organic photoreceptor having a red sensitive layer and a short wavelength sensitive layer, subjecting the imaging member to negative charges, followed by subjecting the imaging member to positive charges, imagewise exposing the member, and developing with a colored developer composition comprising positively charged toner components, negatively charged toner components, and carrier particles; 4,430,402, which discloses a two-component type dry developer for use in dichromatic electrophotography which comprises two kinds of developers, each of which is comprised of a toner and a carrier, and wherein dichromatic images can be formed by developing a positively and negatively electrified electrostatic latent image successively with toners different in polarity and color from each other; 4,594,302 which discloses a developing process for two-colored electrophotography which comprises charging the surface of a photoreceptor with two photosensitive layers of different spectral sensitivities with one polarity, subsequently charging the photoreceptor with a different polarity, exposing a two-colored original to form electrostatic latent images having different polarities corresponding to the two-colored original, developing one latent image with a first color toner of one polarity, exposing the photoreceptor to eliminate electric charges with the same polarity as the first color toner which are induced on the surface of the photoreceptor in the vicinity of the latent image developed by the first color toner, and developing the other latent image with a second color toner charged with a polarity different from that of the first color toner; 4,500,616 which discloses a method of developing electrostatic latent images by selectively extracting colored grains of one polarity from a mixture containing colored grains having opposite polarity to each other in the presence of an alternating field, followed by development of the electrostatic image by the selectively extracted colored grains; 4,524,117 which discloses an electrophotographic method for forming two-colored images which comprises uniformly charging the surface of a photoreceptor having a conductive surface and a photoconductive layer sensitive to a first color formed

on the conductive substance, followed by exposing a two-colored original to form on the photoconductive layer a latent image corresponding to a second color region in the original with the same polarity as the electric charges on the surface of the photoconductive layer; 4,525,447, which discloses an image forming method which comprises forming on a photosensitive member an electrostatic latent image having at least three different levels of potentials, or comprising first and second latent images and developing the first and second latent images with a three component developer; 4,539,281, which discloses a method of forming dichromatic copy images by forming an electrostatic latent image having a first image portion and a second image portion; 4,562,129, which illustrates a method of forming dichromatic copy images with a developer composed of a high-resistivity magnetic carrier and a nonmagnetic insulating toner, which are triboelectrically chargeable; 4,640,883, which discloses a method of forming composite or dichromatic images which comprises forming on an imaging member electrostatic latent images having at least three different potential levels, the first and second latent images being represented, respectively, by a first potential and a second potential relative to a common background potential; 4,045,218 and 4,572,651.

The process of charging a photoresponsive imaging member to a single polarity and creating on it an image comprised of at least three different levels of potential of the same polarity is illustrated in U.S. Patent 4,078,929. This patent discloses a method of creating two-colored images by forming on an imaging surface a charge pattern including an area of first charge as a background area, a second area of greater voltage than the first area, and a third area of lesser voltage than the first area with the second and third areas functioning as image areas. The charge pattern is developed in a first step with positively charged toner particles of a first color and, in a subsequent development step, developed with negatively charged toner particles of a second color. Alternatively, charge patterns may be developed with a dry developer containing toners of two different colors in a single development step. Also of interest with respect to the trilevel process for generating images is U.S. Patent 4,686,163.

Moreover, illustrated in U.S. Patent No. 5075185 are developers, toners and imaging processes thereof. In an embodiment of the copending application, there is provided a process for forming two-color images which comprises (1) charging an imaging member in an imaging apparatus; (2) creating on the member a latent image comprising areas of high, intermediate, and low potential; (3) developing the low areas of potential by, for example, conductive magnetic brush development with a developer comprising carrier particles, and a colored first toner comprised

of resin particles, colored, other than black, pigment particles, and an aluminum complex charge enhancing additive; (4) subsequently developing the high areas of potential by conductive magnetic brush development with a developer comprising a second black developer comprised of carrier particles and a toner comprised of resin, black pigment, such as carbon black, and a charge enhancing additive; (5) transferring the developed two-color image to a suitable substrate; and (6) fixing the image thereto. In an embodiment of the aforementioned U.S. patent, the first developer comprises, for example, a first toner comprised of resin present in an effective amount of from, for example, about 70 to about 98 percent by weight, which resin can be selected from the group consisting of polyesters, styrene-butadiene polymers, styrene-acrylate polymers, styrene-methacrylate polymers, PLIOLITES®, crosslinked styrene acrylates, crosslinked styrene methacrylates, and the like, wherein the crosslinking component is, for example, divinyl benzene, and mixtures thereof; a first colored blue, especially PV FAST BLUE™ pigment present in an effective amount of from, for example, about 1 to about 15 percent by weight, and preferably from about 1 to about 3 weight percent; an aluminum complex charge enhancing additive; and a second developer comprised of a second toner comprised of resin present in an effective amount of from, for example, about 70 to about 98 percent by weight, which resin can be selected from the group consisting of polyesters, styrene-butadiene polymers, styrene-acrylate polymers, styrene-methacrylate polymers, PLIOLITES®, crosslinked styrene acrylates, crosslinked styrene methacrylates, and the like, wherein the crosslinking component is, for example, divinyl benzene, and mixtures thereof; and a black pigment present in an effective amount of from, for example, about 1 to about 15 percent by weight, and preferably from about 1 to about 5 weight percent wherein the aforementioned black toner contains a charge enhancing additive such as an alkyl pyridinium halide, and preferably cetyl pyridinium chloride, and in a preferred embodiment the black toner is comprised of 92 percent by weight of a styrene n-butyl methacrylate copolymer (58/42), 6 percent by weight of REGAL 330® carbon black, and 2 percent by weight of the charge enhancing additive cetyl pyridinium chloride.

Illustrated in U.S. Patent No. 5087538 is a process for forming two-color images which comprises (1) charging an imaging member in an imaging apparatus; (2) creating on the member a latent image comprising areas of high, intermediate, and low potential; (3) developing the low areas of potential by, for example, conductive magnetic brush development with a developer comprising carrier particles, and a colored first toner comprised of resin, a positively charging pigment, and a negatively charging pigment; (4) subsequently developing the high areas of potential by

conductive magnetic brush development with a developer comprising a second developer comprised of carrier particles and a toner comprised of resin, black pigment, such as carbon black, and a charge enhancing additive; (5) transferring the developed two-color image to a suitable substrate; and (6) fixing the image thereto.

Illustrated in copending patent application U.S. Serial No. 705,995, filed May 28, 1991 is, for example, a magneta toner for full color processes, and wherein the toner may contain surface additives such as a mixture of certain colloidal silicas, such as AE-ROSIL#76®, tin oxide, and a polymeric hydroxy compound.

One of the objects of the present invention is to provide a developer with stable triboelectrical toner characteristics which enables the generation of high quality images subsequent to development. A further objective of the present invention is to provide a multicolor image formation wherein the developers are of a specific triboelectric charge, charge distribution, and conductivity, and exhibit acceptable admix times and excellent developer lifetimes.

Accordingly, there is provided a developer composition including a toner and carrier particles, characterized in that said toner comprises resin, carbon black, magnetite, and a charge additive, and a surface additive mixture comprised of a polymeric hydroxy compound and a colloidal silica treated with a quaternary ammonium salt compound; and said carrier particles comprise a core with a polymer mixture coating thereover.

In one embodiment the charge additive is a positive charge enhancing additive and said carrier particles comprise a ferrite core.

The first polymer may be present in an amount of from about 25 percent by weight to about 45 percent by weight, and the second polymer is present in an amount of from about 25 percent by weight to about 55 percent by weight.

The toner resin may comprise styrene polymers, such as, for example, selected from the group consisting of styrene methacrylates, styrene butadienes, and styrene acrylates. Alternatively the toner resin comprises a polyester.

The charge enhancing additive may comprise distearyl dimethyl ammonium methyl sulfate. The semiconductive ferrite carrier core may comprise manganese, copper, zinc, nickel, iron and oxygen.

The first polymer may be present in an amount of from about 40 percent by weight to about 60 percent by weight, and the second polymer is present in an amount of from about 60 percent by weight to about 40 percent by weight.

In one embodiment the ammonium compound is dimethyloctadecyl-3-trimethoxy (silyl)propyl ammonium chloride.

In one embodiment the semiconductive ferrite

core comprises of from about 0.1 to about 20 weight percent of copper, from about zero to about 50 weight percent of magnesium, from about 2 to 25 weight percent of zinc, from about zero to about 12 weight percent of nickel, from about zero to 3 weight percent of manganese, from about 22 to 35 weight percent of oxygen, and from about 40 to 60 weight percent of iron is selected.

In one embodiment carbon black is present in an amount of from about 0.1 to about 0.4 weight percent, and the colloidal silica treated with a quarternary ammonium salt compound is present in an amount of from about 0.8 to about 0.22 weight percent.

In another embodiment the polymeric hydroxy compound is present in an amount of from about 0.1 to about 0.4 weight percent, and the colloidal silica treated with a quarternary ammonium salt compound is present in an amount of from about 0.8 to about 0.22 weight percent.

The ferrite carrier may have a volume median diameter of from about 40 to about 80 microns, and preferably from about 45 to about 60 microns.

In one embodiment the resin comprises an emulsion polymerised styrene butadiene.

One aspect of the present invention is a process for obtaining multicolor, including four-color images, one of which is black, which in an embodiment comprises charging and developing an imaging member four times and wherein a black toner is utilized for one of the images. The aforementioned black toner in one embodiment of the present invention has excellent admix characteristics, for example from about 15 to about 60 seconds as determined by a charge spectrograph, desirable triboelectric properties, for example from about a positive 10 to about 25 microcoulombs per gram as determined by the known Faraday Cage measurement process, acceptable and stable A_t and the like. Another embodiment of the present invention relates to black toners comprised of toner resin particles, black pigment particles, magnetite particles, a charge enhancing additive, and surface additives, such as a mixture of a colloidal silica, AEROSIL #76®, and polymeric hydroxy surface additives, such as UNILINS®, reference U.S. Patent 4,883,736, the disclosure of which is totally incorporated herein by reference, and developers therein as illustrated herein. The black toner of the present invention enables excellent black images with substantially no background deposits, acceptable mottle, minimal image graininess, undesirable history image defects, avoidance or minimization of cometing, improved toner flow characteristics in the developer housing and in the toner dispenser, and moreover this toner is substantially inactive with respect to the colored toners being utilized in that, for example, the triboelectric characteristics and color intensity of the colored toners and developed images thereof is not adversely affected. In embodiments, the toners and developers

of the present invention can be utilized in specific color imaging processes, such as process color, and the like. Other advantages associated with the present invention include the provision of a developer with stable positive triboelectrical toner characteristics which enables the generation of high quality images subsequent to development, that is images with substantially no background deposits and substantially no smearing for a broad range of relative humidity conditions, that is for example from 20 to 80 percent relative humidity at an effective range of temperature zones ranging, for example, from about 50°F to about 120°F, and preferably from about 60 to about 90°F.

An example of the aforementioned development process comprises a developer housing with a twin auger transport single magnetic brush design mounted in the approximate 6 o'clock orientation. The magnetic brush roll (developer roll) is about 30 millimeters in diameter, with a grooved surface for developer transport, and preferably operates at about 3.0 times the speed of the photoreceptor, or imaging member. The developer roll is spaced about 0.5 millimeter from the photoreceptor and is biased with a negative DC bias, for example from 200 to about 500 volts. A stationary magnet is situated internal to the rotating developer roll sleeve, and is comprised of a ferrite with a designed magnetic pole configuration to satisfy the requirements of controlling the developer transport and developability. The developer flow (termed Mass on the Sleeve, or MOS) can be controlled by the location of a low permeability trimmer bar in the magnetic field at the point of trimming. Typically, the MOS is set at from about 25 to about 40 milligrams/cm² and is sensitive to the trim gap, toner concentration (TC) and developer tribo. The twin augers in the developer housing sump transport the developer in opposite directions, first past the toner dispenser, then to the developer pick up region of the developer roll. The augers have slits built into them in order to facilitate the mixing of the fresh toner added to the developer. Usually a number of latent images are formed, such as four, and developed sequentially on the imaging member, first with the black toner of the present invention, magenta toner, cyan toner, and yellow. Also, one can develop black only, or black with one or more other colors.

In another embodiment of the present invention there are provided toners comprised of resin particles, carbon black pigments, such as REGAL 330®, known magnetites, a charge additive like distearyl dimethyl ammonium methyl sulfate, reference U.S. Patent 4,560,635, the disclosure of which is totally incorporated herein by reference, and as surface additives a mixture of UNILIN® and AEROSIL #76®, a colloidal silica treated with a quaternary ammonium compound, such as dimethyloctadecyl-3-trimethoxy(silyl)propyl ammonium chloride available from Tayca Inc. The treated surface additives of U.S. Patent

4,828,954, the disclosure of which is totally incorporated herein by reference, can be selected for the toners and developers of the present invention. This patent discloses toners which contain an inorganic powder that has been subjected to the treatment with a compound having an onium salt structure, see the Abstract, and see columns 2 to 8, and the working Examples.

Also, in another feature of the present invention there are provided developer compositions with excellent electrical characteristics comprised of the black toners illustrated herein and carrier particles preferably comprised of ferrites, especially copper zinc ferrites. One preferred ferrite is described in copending patent application U.S. Serial No. 572,207. In the aforementioned copending application, there is disclosed a semiconductive ferrite core with a coating thereover comprised of a mixture of first and second polymers that are not in close proximity thereto in the triboelectric series, and a ferrite carrier composition with a coating of a first polymer present in an amount of from about 10 percent by weight to about 90 percent by weight, and a second polymer is present in an amount of from about 90 percent by weight to about 10 percent by weight

These and other features of the present invention can be accomplished in embodiments by providing developers, toners and imaging processes thereof. In an embodiment of the present invention, there are provided toner compositions comprised of resin particles, black pigment particles, magnetites, a charge enhancing additive component, and surface additives comprised of a mixture of certain treated colloidal silicas, and polymeric hydroxy compounds, such as UNILIN® components available from Petrolite Corporation. Developers can be prepared by admixing the aforementioned toners with carriers, such as ferrites, and the like, and preferably ferrite carriers, which carriers are coated with a polymer mixture, such as polymethyl methacrylate and KYNAR®, reference U.S. Patents 4,937,166 and 4,935,326.

Examples of resin particles selected for the toners of the present invention include styrene acrylates, styrene methacrylates, polyesters, crosslinked styrene methacrylates, styrene butadienes, especially those with a high, such as from about 80 to about 95 weight percent styrene content, like the commercially available Goodyear PLIOLITES®, PLIOTONES®, and the like. The resin is present in an effective amount of from, for example, about 70 to about 98 percent by weight. Specific toner resins include known styrene acrylates, styrene methacrylates (58/32), linear, and branched polyesters, PLIOLITES®, PLIOTONES® available from Goodyear Chemical Company, styrene-butadiene polymers, particularly styrene-butadiene copolymers wherein the styrene portion is present in an amount of from about 83 to about 93 percent by weight, and prefer-

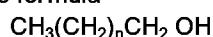
ably about 88 percent by weight, and the butadiene portion is present in an amount of from about 7 to about 17 percent by weight, and preferably about 12 percent by weight. Also suitable are styrene-n-butylmethacrylate polymers, particularly those styrene-n-butylmethacrylate copolymers wherein the styrene segment is present in an amount of from about 50 to about 70 percent by weight, preferably about 58 percent by weight, and the n-butylmethacrylate segment is present in an amount of from about 30 to about 50 percent by weight, preferably about 42 percent by weight. Mixtures of these resins may also be selected. Preferred as the toner resin is an emulsion polymerized styrene butadiene, reference U.S. Patent 4,469,770, preferably present in an amount of about 87 to about 89 percent by weight..

Black toner pigments are known and include carbon blacks like REGAL 330®, VULCAN®, furnace blacks, and the like. The black pigment is present in various effective amounts such as, for example, from about 1 to about 15, and preferably from about 2 to about 10 weight percent of the toner. These pigments are part of a mixture with known magnetites, such as MAPICO BLACK®, and the like. The mixture preferably contains in embodiments effective amounts of carbon black, such as from about 2 to about 10 weight percent, and magnetite, such as MAPICO BLACK®, preferably from about 2 to about 10, and more preferably from about 2 to about 7 weight percent. One preferred mixture is comprised of 5.5 percent by weight of toner of REGAL 330® carbon black and MAPICO BLACK®, 4.5 weight percent.

Examples of charge enhancing additives, which are present in the toner in various effective amounts, such as from about 0.5 to about 10, and preferably from about 1 to about 2 weight percent, include known additives such as distearyl dimethyl ammonium methyl sulfate, cetyl pyridinium halide, especially the chloride, bisulfides, and mixtures thereof in embodiments. Examples of specific charge additives include alkyl pyridinium halides, and preferably cetyl pyridinium chloride, reference U.S. Patent 4,298,672, organic sulfates and sulfonates, reference U.S. Patent 4,338,390, the disclosure of which is totally incorporated herein by reference; distearyl dimethyl ammonium methyl sulfate (DDAMS), the preferred additive; 1.2 percent by weight of the toner as it enables excellent admix characteristic, reference U.S. Patent 4,560,635, and the like. The black toner in embodiments usually possesses a positive charge of from about 5 to about 35 microcoulombs per gram, and preferably from about 8 to about 25 microcoulombs per gram, which charge is dependent on a number of known factors, including the amount of charge enhancing additive present, and the exact composition of the other compositions, such as the toner resin, the pigment, the carrier core, and the coating selected for the carrier core; and an admix time of from

about 15 to about 60 seconds and preferably from about 15 to about 30 seconds. In the preparation of the toner compositions, normally the products obtained comprised of toner resin, pigment, and magnetite, and charge enhancing additive can be subjected to micronization and classification, which classification is primarily for the purpose of removing fines, and substantially very large particles to enable, for example, toner particles with an average volume diameter of from about 8 to about 15 microns, and preferably from about 8 to about 12 microns. The toners of the present invention in embodiments may be prepared by processes such as extrusion, which is a continuous process that comprises dry blending the resin, black pigment, magnetite, and charge control additive, placing them into an extruder, melting and mixing the mixture, extruding the material, and reducing the extruded material to pellet form. The pellets are further reduced in size by grinding or jetting, and are then classified by particle size. In an embodiment of the present invention, toner compositions with an average particle size of from about 8 to about 15, and preferably from 8 to about 12 microns are preferred. The external additive mixtures can then be blended with the classified toner in a known medium intensity dry powder blender. Other known toner preparation processes can be selected including melt mixing of the components in, for example, a Banbury, followed by cooling, attrition and classification.

The aforementioned toners include as surface or external components additives in an effective amount of, for example, from about 0.18 to about 1 weight percent, a mixture of certain colloidal silicas, such as AEROSIL #76®, present in effective amounts of from about 0.8 to about 0.22, and preferably 0.15 weight percent, and a UNILIN® which is a polymeric hydroxy compound of the formula



wherein n is a number of from about 30 to about 300, and preferably n is a number of from about 30 to about 50, present in effective amounts such as from about 0.1 to about 0.4, and preferably 0.25 weight percent. One preferred hydroxy compound has a number average molecular weight of from about 475 to about 1,400, and more preferably a number average molecular weight of from about 475 to about 750. These hydroxy compounds and the toners thereof are illustrated in U.S. Patent 4,883,736. Varying the amounts of these two external additives can enable adjustment of the charge levels of the toners. For example, increasing the amount of AEROSIL #76® and polymeric hydroxy compound generally adjusts the triboelectric charge in a positive direction and improves admix times, which is a measure of the amount of time required for fresh toner to become triboelectrically charged after coming into contact with a developer.

The carrier for the developer in an embodiment of the present invention can be comprised of a ferrite,

preferably copper zinc core, obtained from D.M. Stewart Company, with an average diameter of from about 40 to about 80, and preferably about 45 to about 60 microns volume average diameter, and a polymeric coating thereover of, for example, polyvinylidene fluoride (KYNAR®), and polymethyl methacrylate, with a preferred ratio of 35 to 65, however, a range of about 25 to about 45 for the first polymer like KYNAR®, and about 55 to about 75 for the second polymer like polymethyl methacrylate, 0.15 to about 1, and preferably 0.3 weight percent coating thereover. Preferred carriers that may be selected are the ferrite carriers as illustrated in U.S. Patents 4,937,166 and 4,935,326, and copending patent application U.S. Serial No. 572,207 (D/90196). The aforementioned carriers in one embodiment comprise a core with two polymer coatings not in close proximity in the triboelectric series. The carriers are of a particle size diameter of from about 40 to about 80 microns, and preferably from about 45 to about 60 microns for the semiconductive ferrites.

Examples of imaging members selected for the processes of the present invention include various dielectric or photoconductive insulating material suitable for use in xerographic, ionographic, or other electrophotographic processes, such as layered organic materials as disclosed in U.S. Patent 4,265,990, and the like. The photoresponsive imaging member can be negatively charged, positively charged, or both, and the latent images formed on the surface may comprise either a positive or a negative potential, or both. In one embodiment, four latent images are formed and one of the images is developed with the black toner of the present invention as indicated herein. Known colored toners are selected for the development of the other latent images, which toners include magenta like FANAL PINK®, about 5 percent flushed, cyan, like PV FAST BLUE®, about 2 weight percent, yellow like Permanent Yellow FGL, about 5 percent, and wherein the resin is usually an emulsion polymerized styrene butadiene, although the other toner resins illustrated herein may be used in embodiments. Examples of toners and pigments are illustrated in copending patent applications U.S. Serial Nos. 706,476, 706,477, and 705,995.

The developed images are then transferred to any suitable substrate, such as paper, transparency material, and the like. Transfer may be by any suitable means, such as by charging the back of the substrate with a corotron to a polarity opposite to the polarity of the toner. The transferred image is then permanently affixed to the substrate by any suitable means. For the toners of the present invention, fusing by application of heat and pressure is preferred. There results on a single substrate, such as paper, pictorial colors of black, green, blue, red, yellow, green, brown, and others.

Development is generally accomplished by the

magnetic brush development process disclosed in U.S. Patent 2,874,063. This method entails the carrying of a developer material containing the magnetic toner and magnetic carrier particles by a magnet. The magnetic field of the magnet causes alignment of the magnetic carriers in a brush-like configuration, and this "magnetic brush" is brought into contact with the electrostatic image bearing surface of the photoreceptor. The toner particles are drawn from the brush to the electrostatic image by electrostatic attraction to the undischarged areas of the photoreceptor, and development of the image results. For the process of the present invention, the conductive magnetic brush process is generally preferred wherein the developer comprises conductive carrier particles and is capable of conducting an electric field between the biased magnet through the carrier particles to the photoreceptor.

Developer compositions selected for the present invention generally comprise various effective amounts of carrier and toner. Generally, from about 6 to about 12, and preferably 8.5 percent by weight of developer, and from about 88 to about 94 percent, and preferably 91.5 percent by weight of developer are admixed to formulate the developer. The ratio of toner to carrier may vary depending, for example, on the tribo charge and the like desired. Particle size of the colored toners is generally from about 9 to about 14 microns in volume average diameter, and preferably about 11 microns in volume average diameter in embodiments.

Embodiments of the present invention include a developer composition comprised of a toner comprised of resin, carbon black, magnetite, and a positive charge enhancing additive, and a surface additive mixture comprised of a polymeric hydroxy compound and a colloidal silica treated with a quaternary ammonium salt compound; and carrier particles comprised of a ferrite core with a polymer mixture coating thereover; and a full color imaging process which comprises the formation of a multiplicity of separate latent images on a photoconductive imaging member, subsequently developing one image with a black developer composition, and thereafter sequentially developing the remaining three images with three different toners comprised of resin and a colored pigment other than black, and wherein the toner pigment selected for the second image is dissimilar than the toner pigment selected for the third image, and the toner pigment selected for the third image is dissimilar than the toner pigment selected for the fourth image, followed by transferring each of the developed images to a suitable substrate, and fixing the images thereto.

The following Examples are provided. All parts and percentages are by weight unless otherwise indicated.

EXAMPLE I

A black developer composition was prepared as follows. Eighty nine and eight tenths (88.8) percent by weight of emulsion polymerized styrene butadiene (89/11), 5.5 percent of REGAL 330® carbon black, 4.5 percent by weight of the magnetite MAPICO BLACK®, and 1.2 percent by weight of the charge additive distearyl dimethyl ammonium methyl sulfate were melt blended in an extruder ZSK53 wherein the die was maintained at a temperature of between 130 and 170°C, and the barrel temperature ranged from about 70 to about 150°C, followed by cooling, micronization and air classification to yield toner particles of a volume average diameter size of 9.5 microns. The toner particles were then blended with 0.15 percent by weight of colloidal silica particles treated with dimethyloctadecyl-3-trimethoxy(silyl)propyl ammonium chloride, which is believed to be AEROSIL #76®, treated with POLON MF-50® and available from Tayca Corporation of Japan, and 0.25 percent by weight of UNILIN®, with an average molecular weight of 700, reference Example I of U.S. Patent 4,883,736, the disclosure of which is totally incorporated herein by reference, which UNILIN® was obtained from Petro-lite Corporation. Subsequently, carrier particles were prepared by dry powder coating a 50 micron diameter copper zinc ferrite carrier obtained from Steward Chemical Company, 0.3 percent coating weight, with a mixture of KYNAR®, 35 weight percent, and polymethyl methacrylate, 65 weight percent. A black developer was then prepared by blending 100 parts by weight of the coated carrier particles with 10 parts by weight of the black toner in a Lodige Blender for about 15 minutes at 60 RPM resulting in a developer with a toner exhibiting a triboelectric charge of + 13 microcoulombs per gram as determined in the known Faraday Cage apparatus at a toner concentration of about 8.5 percent. Admix time for substantially uncharged added toner comprised of the same components of the above prepared toner is believed to be about 15 seconds as determined in the known charge spectrograph.

The above black magnetic developer was then incorporated into a full four-color Xerox Corporation 5775™ imaging device, and wherein the device included a magenta toner, a cyan toner, and a yellow toner, and there resulted for 100,000 copies with the same developer charge pictorial and text of black with excellent quality and substantially no background, and red, yellow, blue, green, subsequent to transfer and fixing with heat. The triboelectric charge of the magnetic black toner remained at about 10 to about 15 microcoulombs per gram for the 100,000 developed black images. The imaging member utilized was comprised of an aluminum substrate, thereover a photogenerating layer of trigonal selenium, and a top charge transport of the aryl amine, N,N'-diphenyl-

N,N'-bis(3-methyl phenyl) 1,1'-biphenyl-4,4'-diamine, dispersed in 45 weight percent of a MAKROLON® polycarbonate binder, reference U.S. Patent 4,265,990, the disclosure of which is totally incorporated herein by reference.

EXAMPLE II

A toner and developer are prepared by repeating the procedures of Example I with the exceptions that there is selected as the pigment 12.5 weight percent of flushed HOSTAPERM PINK E™ comprised of 40 percent of pigment, and 60 percent of a styrene butadiene obtained from Goodyear Chemical as PLIO-LITE™, and no MAPICO BLACK®. The triboelectric charge of the toner is + 15 microcoulombs per gram. This toner can be utilized with the toner of Example I and two other colored toners for full color imaging processes as illustrated herein.

Examples of magenta pigments include HOSTAPERM PINK E™, available from American Hoechst, HOSTAPERM PINK EB™, available from American Hoechst, FANAL PINK D4830™, available from BASF, LITHOL RUBINE NBD 4573™, available from BASF, effective mixtures thereof, such as, for example, mixtures of HOSTAPERM PINK EB™ or HOSTAPERM PINK E™ with BASONYL RED 560™, available from BASF. The aforementioned magenta pigment is present in the toner in various effective amounts, such as, for example, from about 0.1 to about 15 weight percent, and preferably from about 1 to about 5 weight percent. Also, in embodiments for the magenta toner about 3.2 weight percent of HOSTAPERM PINK E™ with 0.1 to 0.3 weight percent of BASONYL RED 560™ can be selected per 100 parts of toner.

Similar toners can be prepared by utilizing cyan and yellow pigments in place of the HOSTAPERM PINK™.

Other embodiments and modifications of the present invention may occur to those skilled in the art subsequent to a review of the present application; these embodiments and modifications, as well as equivalents thereof, are also included within the scope of this invention.

Claims

1. A developer composition including a toner and carrier particles, characterised in that said toner comprises resin, carbon black, magnetite, and a charge additive, and a surface additive mixture comprised of a polymeric hydroxy compound and a colloidal silica treated with a quaternary ammonium salt compound; and said carrier particles comprise a core with a polymer mixture coating thereover.

2. A developer composition as claimed in claim 1, characterised in that said charge additive is a positive charge enhancing additive and said carrier particles comprise a ferrite core.

3. A developer composition as claimed in claim 1 or claim 2, characterised in that the polymer mixture includes two polymers not in close proximity in the triboelectric series.

4. A developer composition as claimed in any one of claims 1 to 3, characterised in that the polymer mixture comprises polyvinylidene fluoride and polymethyl methacrylate.

5. A developer composition as claimed in any one of claims 1 to 4, characterised in that the carrier core comprises a semiconductive ferrite.

6. A developer composition as claimed in claim 5, characterised in that the semiconductive ferrite core has a conductivity of from about 10^{-5} to about 10^{-12} mho-cm⁻¹ is selected.

7. A developer composition as claimed in any one of claims 1 to 6, characterised in that the surface additive hydroxy compound has a molecular weight of from about 425 to about 1,400.

8. A method of formulating images which comprises generating an electrostatic latent image on a photoconductive imaging member; thereafter developing this image with a developer composition; subsequently transferring the developed image to a supporting substrate; and thereafter affixing the image thereto, characterised in that the developer composition is as claimed in any one of claims 1 to 7.

9. A full color imaging process which comprises the formation of a multiplicity of separate latent images on a photoconductive imaging member, subsequently developing one image with a black developer composition, and thereafter sequentially developing the remaining three images with toners comprised of resin, and a colored pigment other than black, and wherein the toner pigment selected for the second image is dissimilar than the toner pigment selected for the third image, and the toner pigment selected for the third image is dissimilar than the toner pigment selected for the fourth image, followed by transferring each of the developed images to a suitable substrate, and fixing the images thereto, characterised in that the black developer is as claimed in any one of claims 1 to 7.

10. A developer as claimed in any one of claims 2 to

7, characterised in that the ferrite carrier has a volume median diameter of from about 40 to about 80 microns.

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EUROPEAN SEARCH REPORT

Application Number

EP 92 30 8236

Page 1

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D,Y	EP-A-0 276 147 (XEROX CORPORATION) * column 4, line 41 - column 8, line 15 * * column 7, line 49 - column 8, line 51; claims 1,2,8-10 * ---	1-3,5, 7-9	G03G9/087 G03G9/097
Y	US-A-4 971 882 (DON B. JUGLE) * column 7, line 14 - column 9, line 26 * * column 10, line 7 - line 12 * * column 11, line 40 - column 12, line 47 * ---	1-3,5, 7-9	
Y	DE-A-3 836 388 (KONICA CORP.) * page 10, line 36 - line 45; claims 1-17 * ---	1-3,5, 7-9	
Y	EP-A-0 378 181 (KONICA CORPORATION) * page 5, line 44 - page 7, line 10 * * page 12, line 17 - page 15, line 58 * * page 17, line 25 - line 55; claims 1-10 * ---	1-3,5, 7-9	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
Y	US-A-4 965 158 (ROBERT J. GRUBER ET AL.) * column 4, line 42 - line 62 * * column 6, line 23 - column 7, line 26; claims 1,12,17,18,22 * ---	1-3,5, 7-9	G03G
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The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 12 NOVEMBER 1992	Examiner HINDIAS E.
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 I : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document			

EPO FORM 1503 03.82 (P0401)



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 30 8236

Page 2

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A	US-A-4 912 005 (DONALD J. GOODMAN, JOHN F. KNAPP) * column 4, line 12 - line 63; claims 1,15,30 *	6	
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The present search report has been drawn up for all claims			
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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 L : document cited for other reasons & : member of the same patent family, corresponding document			

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