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(54) One part toner powder composition.

(57) A one-part, flowable, dry, electrostatically attractable toner powder comprising

(a) particles each comprising a blend of from about 30 to 80 parts by weight thermoplastic binder and, correspondingly, from about 70 to 20 parts by weight magnetically responsive material; and

(b) a surface treatment composition comprising 0.1 to 2 parts by weight fluoroaliphatic compound per 100 parts by weight of said particles. The toner powder possesses humidity resistance and improve image quality, particularly in terms of image sharpness.

EP 0 050 987 A1

Croydon Printing Company Ltd.

Claims:

1. A one-part, flowable, dry, electrostatically attractable toner powder comprising

(a) particles each comprising a blend of from about 30 to 80 parts by weight thermoplastic binder and, correspondingly from about 70 to 20 parts by weight magnetically responsive material; and

(b) a surface treatment composition comprising from about 0.1 to 2 parts by weight fluoroaliphatic compound per 100 parts by weight of said particles, said surface treatment composition being attached to the surface of said particles.

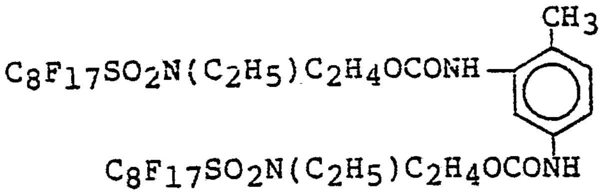
2. A toner powder in accordance with claim 1 wherein said surface treatment composition further comprises from about 0.1 to 2.5 parts by weight silicon dioxide per 100 parts by weight of said particles, said silicon dioxide having an average diameter smaller than said particles.

3. A toner powder in accordance with claim 1 or 2 wherein said surface treatment composition further comprises from about 0.1 to 2 parts by weight carbon per 100 parts by weight of said particles, said carbon having an average diameter smaller than said particles.

4. A toner powder in accordance with claim 1 wherein said fluoroaliphatic compound contains, within a single molecule, both a fluoroaliphatic group and a group which is attracted to said thermoplastic binder.

5. A toner powder in accordance with claim 4 wherein said fluoroaliphatic compound has the formula R_fQ_mZ where R_f is a fluoroaliphatic group, Z is a terminal group, and Q_m is a linking group joining R_f and Z.

6. A toner powder in accordance with claim 5 wherein said fluoroaliphatic compound is selected from the group



$C_8F_{17}SO_2N(C_2H_5)C_2H_4OCONH-C_6H_3(CH_3)-NHCOOC_2H_4N(C_2H_5)SO_2C_8F_{17}$

$(C_8F_{17}SO_2NHC_3H_6N(CH_3)_3^{\oplus})I^{\ominus}$

$C_8F_{17}SO_2N(CH_3)H$

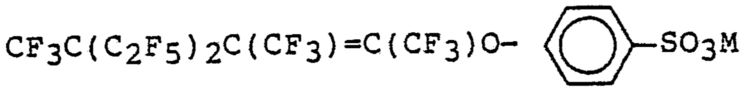
$C_8F_{17}SO_2N(C_2H_5)CH_2COOH$

$C_8F_{17}SO_3K$

$C_8F_{17}SO_2NHC_2H_4NHC_2H_4NH_2$

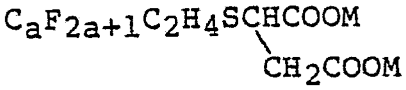
$(C_8F_{17}SON(C_2H_5)C_2H_4)_2POOH$

$C_8F_{17}SO_2N(C_2H_5)C_2H_4OPO(OH)_2$



$CF_3C(C_2F_5)_2C(CF_3)=C(CF_3)O-C_6H_4-SO_3M$

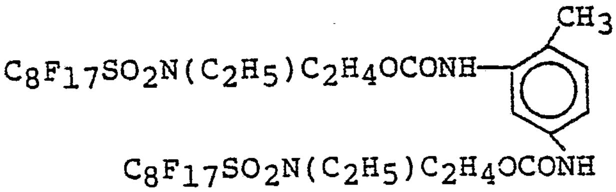
$(C_aF_{2a+1}C_2H_4O)_2P(O)(ONH_4)$



$C_aF_{2a+1}C_2H_4SCH(COOM)CH_2COOM$

where M is hydrogen or a metallic ion.

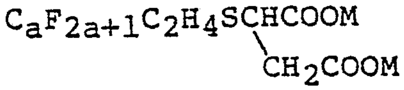
7. A toner powder according to claim 6 wherein said fluoroaliphatic compound is selected from



$C_8F_{17}SO_2N(C_2H_5)C_2H_4OCONH-C_6H_3(CH_3)-NHCOOC_2H_4N(C_2H_5)SO_2C_8F_{17}$

$(C_8F_{17}SO_2NHC_3H_6N(CH_3)_3^{\oplus})I^{\ominus}$

$C_8F_{17}SO_2N(C_2H_5)CH_2COOH$



$C_aF_{2a+1}C_2H_4SCH(COOM)CH_2COOM$

8. A toner powder in accordance with claim 7 wherein said fluoroaliphatic compound is $C_8F_{17}SO_2N(C_2H_5)CH_2COOH$.

9. A method of electrographic recording comprising:

forming a differential image pattern of a one-part, flowable, dry, electrostatically attractable toner powder comprising (a) particles each comprising a blend of from about 30 to 80 parts by weight thermoplastic binder and, correspondingly, from about 70 to 20 parts by weight magnetically responsive material, and (b) a surface treatment composition comprising from about 0.1 to 2 parts by weight fluoroaliphatic compound per 100 parts by weight of said particles, said surface treatment composition being attached to the surface of said particles, thereby adhering said toner powder to said electrostatic image area and thereby developing said electrostatic image area; and

fixing said toner powder by means of heat, pressure, or heat and pressure.

10. A process of preparing a one-part, flowable, dry, electrostatically attractable toner powder comprising:

providing a plurality of particles each comprising a blend of from about 30 to 80 parts by weight thermoplastic binder and, correspondingly, from about 70 to 20 parts by weight magnetically responsive material;

providing a surface treatment composition comprising from about 0.1 to 2 parts by weight fluoroaliphatic compound per 100 parts by weight of said particles;

mixing said particles and said surface treatment composition together at a temperature less than the softening point of said thermoplastic binder for a time sufficient to at least loosely attach said surface treatment composition to the surface of said particles;

heating said particles with attached surface treatment composition to a temperature of about the glass transition temperature of said thermoplastic binder with continued mixing; and

maintaining said heating with continued mixing for a time sufficient to substantially permanently attach said surface treatment composition to said particles thereby providing said toner composition.

11. A toner powder in accordance with claim 4 wherein said fluoroaliphatic compound is polymeric.

Description

ONE-PART TONER POWDER COMPOSITION

Technical Field

This invention relates to dry powder compositions suitable for use in electrographic recording. More particularly, it relates to heat-fusible and pressure-fixable one part toner powders that have a surface treatment comprising a fluoroaliphatic compound attached to the surface of the individual toner powder particles.

Background Art

One-part toner powder formulations (sometimes known as single- or mono-component toners) are known. They differ from two-part or two component developing powders in that they do not utilize a mixture of carrier particles and toner powder particles to make up the developing powder composition. Rather, one-part toner powders are magnetically responsive and do not utilize a carrier to develop the electrostatic image.

One-part toner powders may be either heat-fusible or pressure-fixable. Heat-fusible toner powders are typically fixed after image formation by raising the temperature of the powders to their melting or softening point causing the powder particles to coalesce, flow together and adhere to the substrate. Pressure-fixable toner powders are typically fixed after image formation by simply applying pressure to the powder particles causing them to coalesce and adhere to the substrate.

Although both heat-fusible and pressure-fixable toner powders have been widely used and have enjoyed commercial success, they often suffer from certain disadvantages. For example, the images produced with such powders generally have poor resolution. Thus, they lack sharp edge definition and openings in the images, such as in the letters A, a, B, b, D, d, and O, suffer from "fuzzy-fill-in" (i.e., there is significant toner deposited in such openings thereby rendering them indistinct). Additionally, there is a substantial deposition of toner in non-image areas, i.e., background, particularly the areas between letters. Consequently, the resultant photocopies are messy in appearance and frequently are difficult to read.

Additionally, the flow properties and developing characteristics of such one-part toner powders are often adversely affected by conditions of high humidity. Thus, they may resist flow, e.g., by caking or forming clumps, resulting in streaking on the finished copy. Such caking or clumping may also cause clogging in the development station leading to poor development and transfer of the toner powder and, consequently, poor copy quality.

The foregoing disadvantages are overcome in the present invention by surface treating the toner powder particles with a composition comprising a fluoroaliphatic compound.

Although the use of fluorochemical materials has been disclosed previously, see U.S. Patents 3,798,167; 4,002,570; 4,073,980; 4,139,483; 4,198,477; British Patent 2,034,907; and copending U.S. application serial number 84,607 filed October 15, 1979 and now U.S. Patent 4,268,598, applicant is aware of no disclosure of the use of a treatment composition comprising a fluoroaliphatic compound as a surface treatment for a one-part toner powder.

Of the above-mentioned patents, all except the British Patent and the copending United States application disclose the use of fluorochemical materials with two component developing powder compositions. For example, U.S. Patent 3,798,167 discloses the application of a coating of a fluoropolymer, or optionally, a mixture of a fluoropolymer and a modifying resin, to a carrier material. U.S. Patent 4,002,570 discloses a three component developer composition that comprises carrier particles, toner particles, and a lubricant comprising a particulate, cross-linked polyvinylidene fluoride. The polyvinylidene fluoride particles are said to lubricate and act as effective photoreceptor cleaning materials. U.S. Patent 4,073,980 discloses a two component developing composition wherein the carrier particles have a mixture of a perfluoroacid and molybdenum disulfide coated on their surface. U.S. Patents 4,139,483, and 4,198,477 disclose two-part developer compositions wherein a fluorinated surface active additive is dispersed throughout, rather than coated on, the binder of the toner portion of the composition.

Fluorochemical materials have also been previously utilized with one-part toner powders. Thus, British patent 2,034,907 A (published June 11, 1980) discloses a toner powder having a magnetic material distributed throughout a binder resin. A low molecular weight fluorine-containing surface active agent is applied to the surface of the magnetic material before the magnetic material is distributed throughout the binder.

Copending U.S. application 84,607, filed October 15, 1979, now U.S. Patent 4,268,598, describes a mixture of a sulfonamido surface active material and a toner powder. The resultant mixture has two discrete components, i.e., the surface active material and the toner powder.

Summary of the Invention

In accordance with the present invention, there is provided a one-part, flowable, dry, electrostatically attractable toner powder comprising

(a) particles each comprising a blend of from about 30 to 80 parts by weight thermoplastic binder, and, correspondingly, from about 70 to 20 parts by weight magnetically responsive material; and

(b) a surface treatment composition comprising, from about 0.1 to 2 parts by weight fluoroaliphatic compound per 100 parts by weight of said particles, said surface treatment composition being attached to the surface of said particles.

The toner powder of the present invention produces final images with sharply defined edges, substantially reduced "fuzzy fill-in", and substantially reduced background, even in the areas between images. The most preferred toner of the invention virtually eliminates "fuzzy fill-in", and background. Additionally, the toner of the invention possesses improved flow properties in high humidity conditions. Thus, it does not significantly cake or clump under such conditions and the images produced therefrom have sharp edge definition, exhibit reduced "fuzzy-fill-in", and reduced background.

Still further, the toner powder of the invention tends to be less sensitive to changes in the size of the developing gap utilized than are the previously known one-part toners. Thus, there generally is less decrease in image density as the gap is widened with the instant toners than with such prior art toners. This permits the use of more generous process conditions and machine tolerances, such as doctor blade gap, may be relaxed. The toner of the invention also permits the use of smooth surface developer rolls in place of the more expensive rough surface developer rolls.

The toner powder of the invention also possesses a less positive triboelectric characteristic than does a correspondingly non-surface treated toner powder. It is believed that this property accounts at least in part for the ability of the developing powder compositions of the invention to provide such high resolution images.

Detailed Description of the Invention

The powder of the present invention preferably comprises essentially spherical particles wherein at least 95 number percent of the particles have a maximum dimension in the range of about 4 to 30 microns. Preferably the particles each comprise a blend of from about 35 to 45 parts by weight thermoplastic binder, and correspondingly, from about 65 to 55 parts by weight magnetically responsive material. Most preferably the particles each comprise a homogeneous blend of the binder and magnetically responsive material.

The surprising improvements in copy quality obtained by using the toner powder of the invention is the result of treating the surface thereof so that the treatment composition is attached to the surface of the individual particles. Although the exact mechanism of attachment is not completely understood, it is believed that attachment is achieved by at least partially embedding the mixture into the surface of the particles to provide a layer or zone of the treatment around the particles.

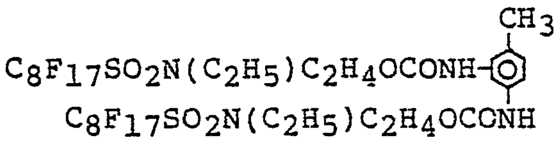
The fluoroaliphatic compound useful as the surface treatment composition may be monomeric or polymeric and, preferably, contains in the same molecule both a fluoroaliphatic group and a group which may contain an aliphatic group, an aromatic group, or both and which is attracted to the thermoplastic binder used in the toner powder of the invention. The particular structure of the fluoroaliphatic compound is not critical to the invention. However, the preferred fluoroaliphatic compound may be represented as R_fQ_mZ where R_f is a fluoroaliphatic group, Q_m is a linking group, and Z is a terminal group.

The fluoroaliphatic group, may be generally described as a fluorinated, monovalent, non-aromatic group of at least 3 carbon atoms. The alphatic chain may be saturated, unsaturated, straight, branched, or, if sufficiently large, cyclic and may include oxygen or trivalent nitrogen atoms bonded only to carbon atoms. A fully fluorinated group is preferred, but hydrogen or chlorine atoms may be present as substituents provided that not more than one atom of either is present for every two carbon atoms, and preferably, the group contains at least a terminal perfluoromethyl group. While fluoroaliphatic groups containing a larger number of carbon atoms will function adequately, those containing not more than about 20 carbon atoms are preferred since larger groups usually represent a less efficient utilization of fluorine than is possible with shorter chains. Fluoroaliphatic groups containing about 5 to 12 carbon atoms are most preferred.

In the linking group Q_m, m is an integer from 0 to 2, and Q represents a direct bond between R_f and Z when m is zero, or a multifunctional, generally difunctional, linking group such as alkylene, arylene, sulfonamido alkylene, carbonamido alkylene and the like. In some instances more than one R_f group may attach to a single Q group and in other instances, a single R_f group may be linked to more than one Q group, or may be linked by a single Q group to more than one Z group.

The Z group represents an anionic, a cationic, a non-ionic or an ampholytic moiety or combinations thereof. Typical anionic groups would include $-CO_2M$, $-SO_2M$, $-SO_3M$, -OPOOM, and $-OP(OM)_2$, where M is hydrogen or a metallic ion, such as sodium, potassium, calcium, etc. Typical cationic groups would include $-NH_2$, -NHR, where R is a lower alkyl group such as methyl, ethyl or butyl, $-NR^1_3{}^{\oplus}A^{\ominus}$, where R^1 is a lower alkyl group or hydrogen and A is an anion, such as iodide, chloride, sulphate, phosphate, hydride, etc. Typical non-ionic groups would include $-NR^2 \rightarrow O$ and those derived from polyethylene oxide and mixed polyethylene oxide-polypropylene oxide polyols. Typical mixed or ampholytic groups would include $-N(C_2H_4OH)_2$, $-NHC_2H_4NHC_2H_4NH_2$, $-N(CH_3)_2C_2H_4CO_2$, $-N(CH_3)(C_2H_4CO_2H)_2 \rightarrow O$, and the like.

Specific examples of useful fluoroaliphatic compounds include



$$\begin{array}{l} \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad CH_3 \\ C_8F_{17}SO_2N(C_2H_5)C_2H_4OCONH-C_6H_3 \\ \qquad C_8F_{17}SO_2N(C_2H_5)C_2H_4OCONH \end{array}$$

$(C_8F_{17}SO_2NHC_3H_6N^{\oplus}(CH_3)_3)I^{\ominus}$

$C_8F_{17}SO_2N(CH_3)H$

$C_8F_{17}SO_2N(C_2H_5)CH_2COOH$

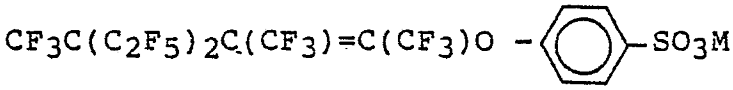
$C_8F_{17}SO_3K$

$C_8F_{17}SO_2NHC_2H_4NHC_2H_4NH_2$

$(C_8F_{17}SO_2N(C_2H_5)C_2H_4O)_2POOH$

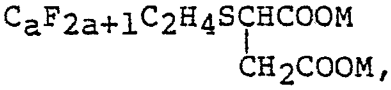
$C_8F_{17}SO_2N(C_2H_5)C_2H_4OPO(OH)_2$

Other specific examples of useful fluoroaliphatic compounds include



where M is as described above, available as "MD 31" from ICI, Ltd.,

$(C_aF_{2a+1}C_2H_4O)_2P(O)(ONH_4)$, where a is an integer of from about 5-25, available as "Zonyl" FSP from E. I. duPont deNemours), and



$C_aF_{2a+1}C_2H_4S\underset{\displaystyle CH_2COOM}{\underset{|}{C}}HCOOM$, where a and M are as described above, available as "Lodyne" S100 from Ciba-Geigy.

Polymeric fluoroaliphatic compounds are also useful in the invention. For example, the copolymer (95/5 by weight) of $C_8F_{17}SO_2N(C_2H_5)C_2H_5OCOC(CH_3){=}CH_2$ and butylacrylate is a useful surface treatment material.

Fluoroaliphatic compounds and methods for their preparation are further described in, for example, United States Patents, 2,559,751; 2,559,749; 2,559,754; 2,559,629; 2,597,702; 2,732,398; 2,759,019; 2,803,615;

2,809,999; 2,915,554; 3,129,254; 3,282,905; 3,398,182; 3,911,056; 4,171,282; British Specifications 1,270,662; 1,130,822; and Organic Fluorine Chemistry, Milas Hudlicky, Plenum Press, N.Y. (1971).

The fluoroaliphatic compound is preferably blended with one or more other ingredients before being applied to the surface of the particles. Thus, the surface treatment may further comprise from about 0.1 to 2.5, preferably 0.5 to 2.5, parts by weight silicon dioxide per 100 parts by weight particles; from about 0.1 to 2, preferably 0.5 to 1, parts by weight carbon per 100 parts by weight particles; or both.

Most preferably the treatment composition comprises a mixture of said fluoroaliphatic compound, said silicon dioxide, and said carbon. In this instance the treatment composition preferably comprises from about 0.5 to 1 part by weight silicon dioxide, 0.4 to 0.7 part by weight fluoroaliphatic compound, and 0.7 to 0.8 part by weight carbon per 100 parts by weight particles when heat-fusing toners are made; and from about 1 to 2.5 parts by weight silicon dioxide, 0.6 to 1.2 parts by weight fluoroaliphatic compound, and 0.7 to 0.8 part by weight carbon per 100 parts by weight particles when pressure-fixing toners are made.

The silicon dioxide useful in the surface treatment comprises a powder having an average particle size (i.e., average diameter) smaller than that of the toner powder particles but whose exact size is otherwise not critical to the invention. Preferably the silicon dioxide is a pyrogenic silica in the form of spherical particles having an average diameter in the range of 5 to 50 millimicrons (most preferably in the range of 10 to 20 millimicrons).

Silicon dioxide particles per se are known and may be prepared by, for example, the hydrolysis of silicon tetrachloride in an oxygen-hydrogen flame. Pyrogenic silicon dioxide is hydrophilic as prepared. However, it can be rendered hydrophobic, if desired, by reacting the silanol groups on the particle surface with chlorosilane.

Examples of useful silicon dioxides include "Aerosil®" 200 (a hydrophilic, pyrogenic, white fluffy powder, 99.8% SiO_2, average primary particle size of 12 millimicron, bulk density of 200 m_2/g, and BET surface area of 200 ± 25 m^2/G), and "Aerosil®" R972 (a hydrophobic, pyrogenic, white fluffy powder, 98.3% SiO_2, average primary particle size of 16 millimicron, bulk density of 60 g/l, and BET surface area of 120 ± 20 m^2/g). These materials are available from Degussa, Incorporated.

The carbon useful in the surface treatment is also a powder whose average particle size (i.e., average diameter) is smaller than that of the toner powder particles but whose exact size is otherwise not critical to the invention. Particularly useful carbons have an average diameter below about 100 millimicrons and preferably one below about 40 millimicrons. It is also preferred that the carbon be conductive, i.e., that it have a static electrical conductivity of at least 10^{-2} reciprocal ohm-cm in a 10,000 v/cm electrical field. Static electrical conductivity may be measured as described in U.S. Patent 3,639,245 at column 3, line 47 - column 6, line 46.

Examples of useful carbon materials include carbon blacks such as "Vulcan" XC-72R, a conductive carbon black with a maximum particle size of 30 millimicron sold by Cabot Corporation; "Conductex" 950, maximum particle size of 21 millimicron sold by Cities Service; "Raven" 1800, maximum particle size of 18 millimicron sold by Columbia Chemicals; "Ketjenblack" EC sold by Noury; and "Thermax" MT sold by R. T. Vanderbilt.

When a conductive carbon is employed in the surface treatment, the resulting toner powder preferably has a dynamic conductivity in the range of 2-15 (most preferably 6-9) microamperes (μA) in an electric field of 1,000 D.C. volts. The dynamic conductivity referred to here is measured according to the technique described hereinafter.

The thermoplastic binder useful in the present invention may be any thermoplastic material although organic materials are preferred. Most preferably the binder is selected from the group consisting of (a) waxes that have a melting point in the range of 45°C to 150°C as measured according to ASTM:D-127, (b) organic resins that have a ring and ball softening point above about 60°C as measured according to ASTM:E-128, and mixtures of the two.

Waxes useful in the binder include aliphatic waxes (e.g., natural or synthetic), fatty acids and derivatives thereof, metal salts of fatty acids, hydroxylated fatty acids or amides, low molecular weight ethylene homopolymers, or mixtures of such materials. Other useful waxes include aromatic and polymeric wax-like materials.

Representative examples of useful aliphatic waxes include paraffin wax, microcrystalline wax, caranauba wax, montan wax, ouricury wax, ceresin wax, candellila wax, and sugar cane wax. Representative examples of useful fatty acids include stearic acid, palmitic acid, and behenic acid. Representative examples of useful metal salts of fatty acids include aluminum stearate, lead stearate, barium stearate, magnesium stearate, zinc stearate, lithium stearate, and zinc palmitate. Representative examples of useful fatty acid derivatives include castor wax (glyceryl tris-12-hydroxy stearate), methyl hydroxystearate (commercially available under the trade name "Paracin 1"), ethylene glycol monohydroxy stearate (commercially available under the trade name "Paracin 15"), and hydroxystearic acid. Representative examples of useful hydroxylated fatty acids or amides include N(betahydroxyethyl)ricinoleamide (commercially available under the trade name "Flexricin 115"), N,N'ethylene-bis-ricinoleamide (commercially available under the trade name "Flexricin 185"), N(2-hydroxylethyl)-12-hydroxystearamide (commercially available under the trade name "Paracin 220"), and N,N'-ethylene-bis-12-hydroxystearamide (commercially available under the trade name "Paracin 285"). Representative examples of ethylene homopolymers include the low molecular weight polyethylenes such as the Bareco "Polywaxes", e.g., "Polywax" 655, 1000, and 2000 sold by the Bareco Division of Petrolite Corporation. Other ethylene homopolymers include oxidized, high density, low molecular weight polyethylenes such as "Polywax" E-2018 and E-2020 sold by Bareco Division of Petrolite Corporation, and the "Epolene" series of low molecular weight polyethylene resins such as "Epolene" E-14 available from Eastman Chemical Products Incorporated. Representative examples of useful aromatic wax-like materials include dicyclohexylphthalate, diphenylphthalate and the "Be Square" series of waxes from the Bareco Division of Petrolite Corporation, such as "Be Square" 195. The "Be Square" waxes are high melting point waxes that consist of paraffins and napthenic hydrocarbons.

Representative organic resins useful as the thermoplastic binder are polyamides, polystyrenes (e.g., 2000 mol. wt.); epoxy resins (e.g., diglycidyl ether of bisphenol-A such as "Epon" 1004, commercially available from Shell Chemical Corp); acrylic resins (e.g., "Elvacite" 2044, and N-butyl methacrylate commercially available from E. I. duPont deNemours); vinyl resins such as polyvinyl butyral (e.g., "Butvar" B72-A, commercially available from Monsanto Company), polyvinyl acetate resins (e.g., "Gelva" V-100, commercially available from Monsanto Company); vinyl copolymers such as vinyl chloride/vinyl acetate (e.g., "VYHH", commercially available from Union Carbide Corp.), ethylene/vinyl acetate copolymers; cellulose esters such as cellulose acetate butyrate (e.g., "EAB-171-25", commercially available from Eastman Chemical Products, Inc.), cellulose acetate propionate; and cellulose ethers.

When a heat-fusible developing powder is desired, the thermoplastic binder preferably comprises the organic resin. Most preferably the organic resin is an epoxy resin. However, some wax may also be incorporated into the binder of a heat-fusible toner powder. The wax is added to reduce the temperature necessary to achieve satisfactory fusing of the toner to a desired surface. Typically the weight ratio of the organic resin to the wax is between about 4:1 and 20:1.

When a pressure fixable developing powder is prepared, the thermoplastic binder comprises either the wax alone or a combination of the wax and the organic resin. When the binder comprises said combination, the weight ratio of wax to organic resin is between about 1:1 to 50:1, preferably between about 4:1 and 20:1. Most preferably the binder consists essentially of the wax. In either event, the wax preferably is selected from microcrystalline wax, low molecular weight polyethylene resin, or a combination thereof, while the organic resin, when present, comprises an epoxy resin.

The magnetically responsive material employed in the developing powder composition preferably is homogeneously distributed throughout the binder. Additionally, it preferably has an average major dimension of one micron or less. Representative examples of useful magnetically responsive materials include magnetite, barium ferrite, nickel zinc ferrite, chromium oxide, nickel oxide, etc.

Other binders useful for pressure-fixable toner powders are known. Thus, for example, see U. S. Patent 3,965,022. This patent describes a binder that comprises (a) about 74 to 98 parts by volume of a thermoplastic component that has a softening point of at least about 60°C, a 10-second shear creep compliance in the range of about 1×10^{-9} cm^2/dyne to 1×10^{-13} cm^2/dyne at room temperature, and a "heat deflection temperature" below about 300°C, and (b) about 2 to 26 parts by volume of a non-volatile component having a principal glass transition temperature below about 0°C as measured by differential thermal analysis, and a 10-second shear creep compliance in the range of about 50 $cm^2/dyne$ to 8 x 10^{-8} $cm^2/dyne$ at room temperature, said non-volatile component preferably being elastomeric.

Examples of useful thermoplastic components (i.e., low shear creep compliance materials) and of non-volatile components (i.e., high shear creep compliance materials) are disclosed in U.S. 3,965,022. The disclosures of that patent are incorporated herein by reference for the disclosure of the binder system.

Other ingredients may be incorporated onto the particles used in the toner powder of the invention. Thus, fatty acid amides containing at least about 10 carbon atoms have been found to be useful in reducing the time required to prepare the toner powders. Typically from about 0.05 to 2% by weight of the fatty acid amide is satisfactory. Examples of useful fatty acid amides include erucamide, stearamide, behenamide, oleamide, N,N'-ethylene-bis(tall oil)amide, and N,N'-ethylene-bis-oleamide.

The developing powders of the invention may be readily prepared. Thus, a dry blend of the thermoplastic binder and the magnetically responsive material is obtained by melting the thermoplastic binder, stirring in the magnetically responsive material, preferably until a homogeneous mixture is provided, allowing the mixture to cool, grinding the mixture to form particles, and classifying the resulting solid particles to the desired size (i.e., 1 to 40 microns maximum dimension).

The particles, which are irregularly shaped, are then preferably formed into "prespheres" by first aspirating them into a moving gas stream, preferably air, thus creating an aerosol, and directing the aerosol at an angle of about 90° ± 5° through a stream of gas, again preferably air, which has been heated to about 450°C and

600°C into a cooling chamber where the now substantially spherical particles settle by gravity as they cool.

The surface treatment composition is then applied to the "prespheres". When the treatment composition contains ingredients (e.g., silicon dioxide and/or carbon) other than the fluoroaliphatic compound, a mixture of the ingredients is first prepared by charging them to, for example, a "Waring" blender and mixing for about one-half hour at a medium speed. The resulting preferably homogeneous mixture is fluffy and black.

The prespheres and surface treatment composition are then each added to a blender (e.g., a twin shell blender from "Patterson Kelly") and cold blended a temperature less than the softening point of the thermoplastic binder (e.g., 20-30°C) until the surface treatment is at least loosely adhered to the prespheres. Typically this is accomplished within three hours. If desired, the prespheres may be cold blended with one of the above disclosed fatty acid amides before treating the prespheres with the surface treatment composition.

In either event, the treated prespheres are then "hot" blended at about the glass transition temperature of the thermoplastic binder for a time sufficient to substantially permanently attach the treatment composition to the particles. This is typically accomplished in from two to six hours. Preferably the surface treatment composition is attached as a layer or zone at or near the surface of the prespheres.

After hot blending, the resultant toner powder is cooled for about one half hour, screened to remove agglomerates, and classified so that 95% by weight of the product is greater than 4 microns average diameter and only 5% by weight is greater than 30 microns average diameter.

The toner powder of the invention is useful in electrographic recording processes where a differential image pattern of the toner is formed and subsequently fixed by means of pressure, heat, or heat and pressure. The differential image pattern may be formed by, for example, forming electrostatic image areas on a photoconductive surface ad contacting the image areas with the toner. Alternatively, the differential image pattern may be formed by contacting a passive dielectric surface with the toner; forming the image pattern by, for example, selectively exposing the uniformly toned surface to a stylus which imagewise transmits an electrical potential signal; and magnetically removing toner from uncharged areas. See U.S. Patent 3,816,840 for further description of this process. If desired, the toned image areas may be transferred to another surface prior to fixing.

The present invention is further illustrated by means of the following examples wherein the term "parts" refers to parts by weight unless otherwise indicated.

In these examples, several physical characteristics of the toner powders were measured. The techniques for measuring these characteristics are described below.

a. Dynamic Conductivity.

This property simulates the electrical conductivity of a toner powder when used in an electrostatic copying process. Dynamic conductivity is measured on a test rig that comprises the developing station of a "Secretary III" photocopier (available from the 3M Company) except that the photoconductor drum is replaced by an aluminum drum (12.5 cm dia). The developer roll comprises a stainless steel shell (3.15 cm dia) around an 8 pole circular magnet. A doctor blade, a toner hopper, and a 1000 volt power supply are also supplied. The gap between the developer roll and the aluminum drum is set at 0.071 cm; the gap between the doctor blade and the toner hopper at 0.05 cm; and the gap between the toner hopper and the developer roll at 0.125 cm.

To measure conductivity, 16 ml of toner is charged to the hopper, and the test rig is started so that the developer roll and the aluminum drum are driven in opposing directions with the developer roll having a surface speed of 61.3 cm/sec and the aluminum drum having a surface speed of 19.5 cm/sec. The test rig is then run for five minutes after which the current passing through toner is measured while the toner is in the development gap and under a 1000 volt potential.

b. Maximum Density (D_{max})

This property illustrates the optical output density of an image produced from an original having an optical input density of one. Preferably D_{max} is at least one.

D_{max} is measured by determining the diffuse reflection optical density of the image using a conventional diffuse reflection densitometer (e.g., MacBeth Quanta-Log Diffuse Reflection Densitometer, Model RD-100). The optical density reading is taken as the D_{max} for the toner powder being tested.

c. Density Decay.

This property measures the sensitivity of a toner powder to changes in the size of the development gap. Generally speaking, the density of an image produced from a given toner powder decreases as the size of the development gap increases. Thus the larger the gap, the lower the resultant image density. Larger decreases indicate that the toner powder is more sensitive to such changes and, therefore, requires narrower development gaps.

Density decay is measured on a conventional electrographic recording device (e.g., a "Secretary III") as follows. The development gap is reduced to the point at which image densities on an imaged and developed photoconductive surface vary from bands of high and low image density horizontally across said photoconductive surface. The development gap is then opened by turning the adjustment means two full turns from this point. A copy is produced at this opening and its image density measured using a conventional diffuse reflection densitometer such as is set forth above. The development gap is then further opened by turning the adjustment means four additional (total of six) turns from said point. A copy is produced at this opening and its image density measured as described above. The density decay is taken as the decrease in image density from the narrower to the wider of the two development gaps.

d. Contrast (Gamma).

This property is a measure of a toner powder's ability to distinguish between differing image densities on an original and reproduce those differences on a copy. High contrast values, i.e., greater than 5, indicate the toner powder's inability to distinguish and reproduce the difference between varying image densities.

Contrast is measured according to the following procedure. Copies of an original having a range of image densities (i.e., a step wedge) are made on an electrographic recording (e.g., a "Secretary III") machine. The output image densities are measured as described above in the D_{max} test and plotted against the $\log_{10}$ of the input image densities. The $\log_{10}$ of the input densities are plotted as the horizontal axis and the output densities are plotted as the vertical axis. The contrast (gamma) is taken as the slope of the straight line portion of the plot.

Examples 1-16

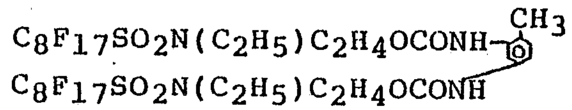
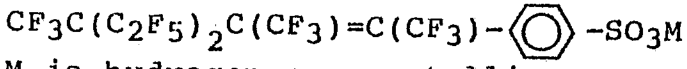
A series of examples of heat fusible toner powders were prepared. In the examples, 95% by weight of the toner powders were greater than 5 microns average diameter and only 5% by weight were greater than 22 microns average diameter. Examples 1-15 were examples of the invention while Example 16 was a toner powder that was not surface treated.

In each example the prespheres were prepared as described above from 40 parts epoxy resin ("Epon" 1004 from Shell Chemical Company) and 60 parts magnetite.

Examples 1-14 the prespheres were separately surface treated as described above using different treatment compositions. In example 15 the surface treatment composition was cold blended with the prespheres for 15 hours prior to hot blending.

The following treatment compositions, with quantities reported as parts, were used:

TREATMENT COMPOSITIONS

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
 $C_8F_{17}SO_2N(C_2H_5)C_2H_4OCONH$- CH_3 $C_8F_{17}SO_2N(C_2H_5)C_2H_4OCONH$	0.6	--	--	--	--	--	--	--	--	--	--	--	--	--	--
$(C_8F_{17}SO_2NHC_3H_6N^{\oplus}(CH_3)_3)I^{\ominus}$	--	0.6	--	--	--	--	--	--	--	--	--	--	--	--	--
$(C_8F_{17}SO_2N(C_2H_5)C_2H_4)_2POOH$	--	--	0.6	--	--	--	--	--	--	--	--	--	--	--	--
$C_8F_{17}SO_2N(C_2H_5)C_2H_4OPO(OH)_2$	--	--	--	0.6	--	--	--	--	--	--	--	--	--	--	--
$C_8F_{17}SO_2N(C_2H_5)CH_2COOH$	--	--	--	--	0.6	0.6	0.6	0.6	0.6	--	--	--	--	0.6	0.6
$C_8F_{17}SO_2N(CH_3)H$	--	--	--	--	--	--	--	--	--	0.6	--	--	--	--	--
$C_8F_{17}SO_3K$	--	--	--	--	--	--	--	--	--	--	0.6	--	--	--	--
$(C_aF_{2a+1}C_2H_4O)_2P(O)(ONH_4)$ ("Zonyl" FSP)	--	--	--	--	--	--	--	--	--	--	--	0.6	--	--	--
 $CF_3C(C_2F_5)_2C(CF_3)=C(CF_3)$- -$SO_3M$ M is hydrogen or a metallic ion such as Na ("MH-31")	--	--	--	--	--	--	--	--	--	--	--	--	0.6	--	--
"Aerosil" 200	0.8	0.8	0.8	0.8	0.8	0.8	--	--	--	--	0.8	0.8	0.8	0.8	--
"Aerosil 972"	--	--	--	--	--	--	0.8	0.8	--	0.8	--	--	--	--	--
"Vulcan" XC-72R	0.7	0.7	0.7	0.7	0.7	--	0.7	--	0.7	0.7	0.7	0.7	--	--	--
"Conductex" 950	--	--	--	--	--	0.7	--	0.7	--	--	--	--	--	--	--

The non-surface treated toner powder (Example 16) was prepared by combining 100 parts of the prespheres with 0.6 parts of conductive carbon black (Vulcan XC-72R from the Cabot Corporation) to form a mixture. The mixture was dry blended at room temperature for 3 hours and then hot blended at 65°C for about 8 hours. The carbon was then embedded into the prespheres as a layer or zone at or near the surface thereof by drawing the particles of the mixture into an air stream at a rate of 36 kg/hr to form an aerosol; directing the aerosol at 90° ± 5° into a hot (650°C) air stream; allowing the powder to settle; and collecting the powder by filtration. About 0.05% by weight SiO_2 ("Aerosil" 972, Degussa, Incorporated) was blended with the toner as a separate component to aid its flow properties.

The powders were then used in a heat-fusing copying process in a "Secretary III" copying machine (available from the 3M Company) to provide images on plain paper substrates. The exposure voltages are reported in Table 1. The bias voltage was set at -200 DC volts.

The surface treatment compositions employed together with the results obtained (i.e., dynamic conductivity of the toner powders, the maximum density (D_{max}), the density decay, and the image contrast) are given in Table 1.

TABLE 1

Example	Treatment Composition	Exposure Voltage	Dynamic Conductivity ($\mu A/10^3 v$)	Dmax	Density Decay	Contrast
1	A	77	9.8	1.06	0.26	2.4
2	B	75	8.8	0.89	0.24	1.2
3	C	82	7.1	1.18	0.26	3.4
4	D	82	6.7	1.19	0.23	3.8
5	E	79	7.1	1.17	0.23	3.0
6	F	77	6.3	1.15	0.30	3.0
7	G	79	8.7	1.1	0.32	3.2
8	H	80	8.4	1.15	0.24	3.0
9	I	83	7.0	1.17	0.22	3.1
10	J	79	7.9	1.12	0.27	2.1
11	K	80	9.7	1.02	0.22	1.8
12	L	79	8.3	1.07	0.23	2.2
13	M	77	9.3	1.05	0.25	1.5
14	N	78	2.0	1.44	0.13	5.0
15	O	76	2.7	0.85	0.38	1.55
16	None	79	6.4	1.18	0.36	2.6

The toner powders of the invention, i.e., those used in Examples 1-15 provided copies with images that were more sharply defined than were the images provided by the toner used in Example 16. Thus the edges of the images produced in Examples 1-15 were sharp, the openings in the images (letters) had substantially reduced "fuzzy fill-in", and the spaces between the images (background) had substantially reduced blurring caused by undesired toner deposition. Furthermore, the toners used in Examples 1, 2, 7, and 13 produced copies having virtually no "fuzzy fill-in" and virtually no background. The images produced from the toner used in Example 16, however, had blurry edges, substantial "fuzzy fill-in", and substantial background.

Additionally, the toners of the invention generally demonstrated less density decay than did the non-surface treated toner used in Example 16. Thus, the toners of the invention generally permit the use of less stringent process conditions such as gap latitude.

The foregoing results are achieved without adversely affecting other physical characteristics of the toner powders. Thus, dynamic conductivity, D_{max}, and contrast all remain within acceptable limits.

EXAMPLE 17

A pressure-fixable toner powder according to the invention was prepared as described above except that the prespheres were prepared from 10 parts "Polywax" 1000 (a low molecular weight, unmodified homopolymer of ethylene having a Mw/Mm of 1.2 from Bareco Division of Petrolite Corporation), 30 parts "Epolene" E-14 (an emulsifiable low molecular weight polyethylene resin from Eastman Chemical Products, Incorporated), and 60 parts Magnetite.

The prespheres were surface treated as described above with a treatment composition comprising 0.6 parts "Vulcan" XC-72R, 2.4 parts "Aerosil" 200, and 1.2 parts $C_8F_{17}SO_2N(C_2H_5)CH_2COOH$.

The resulting toner powder was used in a cold (room temperature) pressure-fixing copying process to provide images on a plain paper substrate. The exposure voltage was 82 volts. The images on the copies produced were sharp, the openings in the images had virtually no "fuzzy fill-in", and there was virtually no background.

The toner powder had a dynamic conductivity of 5.3 $A/10^3V$, a D_{max} of 1.47, and a contrast (gamma) of 4.3.

EXAMPLE 18

A heat-fusible toner powder according to the invention was prepared as described in Examples 1-14 utilizing the following surface treatment composition:

$C_8F_{17}SO_2NHC_2H_4NHC_2H_4NH_2$	0.6 parts
"Aerosil" 200	0.8 parts
"Vulcan" XC-72R	0.7 parts

The resulting toner powder was used in a heat-fusing copying process in a "Secretary" III copying machine to provide images on plain paper substrates. The exposure voltage was 75 volts and the bias voltage was 200 volts.

The images on the resultant copy were sharply defined, had virtually no "fuzzy fill-in", and the copy had virtually no background. Additionally, the toner powder had a dynamic conductivity of 9.5 $A/10^3V$ and produced images having a D_{max} of 0.62 and a contrast of 0.65. While the D_{max} and contrast values of this example are low, it still demonstrates improved edge sharpness, "fuzzy fill-in" and background.

EXAMPLE 19

A heat fusible toner according to the invention was prepared as described in Examples 1-14 except that the surface treatment composition was prepared by the following procedure.

A dispersion of a polymeric fluoroaliphatic compound in solvent was provided. The fluoroaliphatic compound was a 95/5 by weight copolymer of $C_8F_{17}SO_2N(C_2H_5)C_2H_4OCOC(CH_3)=CH_2$ and butyl acrylate. Sufficient methyl alcohol was added to the dispersion to precipitate the polymer. The polymer was dried in a vacuum oven. The fluoroaliphatic compound was then ground with a mortar and pestle to reduce it to a relatively fine powder.

The surface treatment composition was then prepared as described above by combining 0.6 part fluorochemical, 0.8 part "Aerosil" 200, and 0.7 part "Vulcan" XC-72 R.

The resulting toner powder was used in a heat-fusing copying process in a "Secretary" III copying machine to provide images on plain paper substrate. The exposure voltage was 78 volts and the bias voltage was 200 volts.

The images on on the resultant copy were sharply defined, had virtually no "fuzzy fill-in", and the copy had virtually no background. Additionally, the toner powder had a dynamic conductivity of $8 \mu A/10^3 V$ and produced images having a D_{max} of 0.98 and a contrast of 1.53.

European Patent Office

EUROPEAN SEARCH REPORT

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EP 81305059.8

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
D,X	GB - A - 2 034 907 (KONISHIROKU PHOTO) (11-06-1980) * Page 1, line 62 - page 2, line 55; claims 1-6 * --	1,3-5, 9,10
	CA - A - 971 026 (CROOKS) * Claims 1-9 * ----	1,3-5

CLASSIFICATION OF THE APPLICATION (Int. Cl.³)

G 03 G 9/08
G 03 G 13/16

TECHNICAL FIELDS SEARCHED (Int. Cl.³)

G 03 G

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: 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	21-01-1982	SALTEN

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