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(54) Toner compositions.

(57) A thermally fixable electrostatographic toner composition contains toner particles which have small particles strongly adhered to their surfaces in a uniform distribution. These small particles are applied to the toner surfaces from aqueous dispersions. The toner particles so coated have lower charge than the uncoated starting toners and show excellent transfer properties and imaging performance. The aqueous dispersion of small particles can additionally contain charge agents that are applied to the toner particle surfaces simultaneously with the small particles.

This invention relates to electrostatographic toner and developer compositions and, more particularly, to coated toners and a method for making same, such toners having improved charging and transfer properties.

The transfer properties of toners represent a major limitation on the image quality obtainable from present electrographic products. Poor transfer to the receiver sheet results in a high level of toner remaining on the photoconductive surface in copy machines, leading to images of poor uniformity and low density, and of increased sensitivity to the smoothness of the image receiving sheet. The problem is especially serious with toners of small particle size, which are desirable for high image resolution.

The charging characteristics of electrographic toners are also of serious concern in toner formulation. These characteristics control the behavior in the developer station, as well as the toning process and the transfer process. Organic and metalorganic compounds have been used as charge agent additives for the purpose of controlling the amount of electrostatic charge on toner particles ever since the earliest toners were made. The usual process for their incorporation into the toner is to melt-blend them into the toner polymer during the compounding process of toner manufacture. The charge agent is normally utilized at levels of 0.5 to 5% by weight, based upon the toner polymer. Some of these charge agents are expensive chemicals. The only portion of the charge agent which is effective is that on the surface of the toner, since it is the toner surface that contacts the carrier particles in a developer as well as the photoconductive layer. In addition, these charge agents are often difficult to disperse uniformly in the toner, resulting in poor developer behavior, including dusting, short developer life, and erratic charge levels.

Numerous efforts have been made to improve the powder flowability, fixability, and triboelectric characteristics of toners by the addition of small particles of various materials, such as resins, pigments, and inorganic oxides. U.S. Pat. 4,803,144, for example, discloses toner particles that contain on their surface a powder of SnO_2 or of a combination of SnO_2 with other inorganic oxides such as ZnO, TiO_2, SiO_2, and the like. U.S. Pat. 4,513,074 discloses colloidal silica particles as an external additive. Similarly, the addition of hydrophobic silica to improve the flowability, triboelectrification, and other properties of toners is described in U.S. Pat. Nos. 4,623,604 and 4,797,339 and in Japanese Kokais 54051844 and 62237463.

U.S. Pat. 4,301,228 discloses a triple component development material of toner particles, carrier particles, and electrically insulative fine particles of metallic oxides, such as silica or alumina, which are charged by frictional contact with the toner particles.

Toner compositions containing hydrophobic silica particles of 1-100 nm size in physically dispersed particulate form are disclosed in G.B. 2,166,881-A, and Japanese Kokai 63256967 describes insulating particles made of colloidal or hydrophobic silica and polyvinylidene fluoride on the surface of the toner. Also, Japanese Kokai 01237561 discloses the addition of fine silica powder with aminosilane on its surface to toner particles to give a stable charge.

U.S. Pat. 4,965,158 discloses a toner composition of resin particles, pigment particles, and a surface additive that comprises a charge enhancing component that has been sorbed on a flow agent such as colloidal silica, aluminum oxide, talcs, clays and the like. U.S. 4,937,157 discloses water-insoluble quaternary ammonium bisulfate charge enhancing additives that can be applied to the surface of flow aids such as colloidal silica.

In the above described disclosures, the small particles are understood to be dry blended with the toners and, consequently, weakly adhered thereto. This technique produces dust that deposits on the photoconductor surface and also adversely affects the stability of the developer.

Other recent patents describe the embedding of small particles in the surface of toners. U.S. Pat 4,950,573 discloses the embedding of small organic polymeric particles in thermofusible toner particles for low temperature fixing capability. U.S. Pat. 4,900,647 describes a process for embedding modifier particles in toner particles, using a mechanical impact force. However, these processes can cause the surface particles to be embedded to varying depths and also to be unevenly distributed over the toner particles, as a result of accumulation in depressions and crevices on the toner surface. Such mechano-fusion processes also cause heating of the toner particles, which can lead to their agglomeration. Furthermore, these processes require that the small particles of additive be in a non-agglomerated dry state, a condition often difficult to achieve with particles that have diameters of 0.1 μm or less.

It has now been discovered that the transfer properties of toners can be improved and that the problems encountered in coating toner particles with dry additives of very small particle size can be overcome by coating the toners with aqueous dispersions or solutions of the small additive particles. It has also been found that these aqueous dispersions can additionally contain charge agents that are applied to the toner particle surfaces simultaneously with the small additive particles.

The thermally fixable electrostatographic toner compositions of the present invention comprise toner particles of a thermoplastic resin, said toner particles having upon their surfaces a coating of small particles which can be applied from an aqueous dispersion in a uniform distribution and are strongly adhered to the toner particles. The toner compositions prepared in accordance with the invention possess very good transfer properties, with excellent uniform density patches and high image quality on various image receiving materials. In some embodiments of the invention, the toner particles also have on their surfaces a charge agent that is applied simultaneously with the strongly adhered small particles.

The method of the present invention for making a thermally fixable electrostatographic toner composition comprises the steps of a) mixing an aqueous dispersion of small particles with toner particles of a pigmented thermoplastic resin, b) agitating the resulting mixture of toner particles and small particles to ensure uniform distribution, and c) drying the resulting toner composition. The small particles contained in the aqueous dispersion are preferably colloidal silica, aluminum oxide, or particles of a latex polymer. In some embodiments, the aqueous dispersion of small particles also contains a charge agent.

The described toners are especially suitable for use in two-component developer compositions which comprise magnetic carrier particles and the novel toner compositions.

The method of the present invention enables the use of materials as toner additives that are not readily available in a dry, non-agglomerated state. The particles, which can be either inorganic or polymeric organic substances, are coated in a uniform distribution over the toner surfaces, to which they adhere securely and are not readily dislodged. In addition, the utilization of aqueous compositions for the coating of toner particles in accordance with the method of the invention is especially well suited for efficient continuous manufacturing processes.

Coated toner particles prepared by the method of the invention show greatly improved transfer properties, producing image densities that are both higher and more uniform than those obtained from non-coated toners. In particular, a combination of yellow, magenta, and cyan toners that have been coated by the method of the present invention give darker, more neutral three-color black images than those from non-coated colored toners, which are mottled and bluish.

These beneficial results are at least in part the consequence of improved gap-jumping performance by toner particles prepared by the method of the invention. This improvement in gap-jumping also results in the production of equivalent, high quality images on both rough bond paper and on smoother paper. Non-coated toners typically give inferior images on bond paper. The toners prepared in accordance with the method of the present invention also require considerably lower transfer currents than non-coated toners to produce good results.

Unlike the addenda particles that are dry blended with toners in the prior art, the small particles that are coated from aqueous dispersions on toner particles in accordance with the present invention are uniformly distributed over the toner particle surfaces and are strongly adhered to, but not embedded in, those surfaces. These small particles cannot be dislodged from the toner surfaces even by vigorous agitation of a suspension of coated toner particles with an ultrasonic disperser. This strong adhesion of the small particles to the toner surfaces prevents problems of scumming on the photoconductive layer or contamination of the fusing roll.

In general, any polymer of the type known to the art that is suitable for use in toner particles can be used as the matrix or continuous phase of toner particles used as starting materials in the practice of the present invention. Polymers employed in toner particles of this invention generally have glass transition temperatures (Tg) in the range of 50 ° C to 120 ° C and fusing points in the range of 105 ° C to 200 ° C so that the toner particles can be readily fused to receiving sheets, such as paper, or the like. Presently preferred Tg's are in the range of 50 ° C to 80 ° C and presently preferred fusing points are in the range of 105 ° C to 155 ° C. However, polymers with higher Tg's and higher fusing points can be employed when desired for particular receiving sheets, such as metal plates, or the like.

The term "fusing point" as used herein refers to the temperature at which the toner begins to flow when under the pressure normally encountered in the nip of a toner fusing roll. The term "glass transition temperature", or "Tg", as used herein refers to the temperature at which a polymer changes from a glassy to a rubbery state. Tg can be measured by differential thermal analysis as disclosed in Techniques and Methods of Polymer Evaluation, Vol. 1, Marcel Dekker, Inc., N.Y., 1966.

Preferred polymers are polyesters and polyesteramides. The polyester polymers used as the matrix phase in starting toner particles employed in the practice of this invention preferably have inherent viscosities in the range of 0.05 to 0.80 when measured at a concentration of 0.25 gm/1 at 25 ° C in dichloromethane.

Other suitable polymers for use in toner particles include copolymers of styrene or substituted styrenes and a comonomer such as an acrylic monomer, for example, styrene/butyl acrylate copolymer; polycarbonates; modified alkyl resins; phenolformaldehyde resins; and the like.

In general, methods for manufacturing such polymers are well known, and any convenient preparation procedure can be utilized. For example, in the case of the preferred polyesters, monomers present in a polymerizable monomer mixture are usually dicarboxylic acids and diols, or their functional equivalents. Functional equivalents, for example, in the case of dicarboxylic acids include esters, anhydrides, acid halides, and the like. Examples of dicarboxylic acids and their functional equivalents include terephthalic acid, isophthalic acid, sulfoisophthalic acid, glutaric acid, dimethyl terephthalate, dimethyl glutarate, phthalic anhydride, and the like. Examples of suitable diols include ethylene glycol, 1,2-propanediol, neopentyl glycol, 1,4-cyclohexanedimethanol, and the like. Also useful are polyfunctional compounds having two or more carboxyl groups or two or more hydroxyl groups per molecule. Various polyols, such as triols, tetrols, or various polyacids, can be used to create branching in the polyester chain, such as glycerol, pentaerythritol, trimethylolpropane, trimellitic anhydride, pyromellitic dianhydride, and the like. Preferably, up to 10 mole percent of a reactable monomer mixture is comprised of a compound having three or more hydroxyl and/or carboxyl groups. Polymerization procedures are well known in the art. Branched polyester resins can be prepared, for example, by using two stage polyesterification procedures, such as described in U.S. Pat. Nos. 4,140,644 and 4,217,400.

The starting toner particles for toner compositions prepared by the method of the invention can be made from polymers by known procedures. By one procedure, a thermoplastic or thermosetting solid polymer, optionally with any desired additives such as a colorant (dye or pigment) or a charge agent (including an antiblocking agent), is melt blended on heated compounding rolls or in a melt extruder until a uniform composition is obtained wherein the polymer comprises at least 50 weight percent, and preferably, 75 to 98 weight percent, of a product composition, with the balance up to 100 weight percent thereof being such additives. The concentration of colorant can range between 0.5 to 20 weight percent, more preferably 1 to 6 weight percent, and the amount of charge control agent, can range between 0.05 to 5 weight percent, more preferably 0.3 to 2.0 weight percent.

The toner particles can be either positively or negatively chargeable. Positively chargeable particles are preferred. Examples of useful charge agents are disclosed in U.S. Pat. Nos. 3,893,935; 4,079,014; and 4,323,634; and in British Pat. Nos. 1,501,065 and 1,420,839. Quaternary ammonium salt charge agents are disclosed in "Research Disclosure No. 21,030", Vol 210, October, 1981 (published by Industrial Opportunities Ltd., Homerwell, Havant, Hampshire, PO9 1EF, United Kingdom.) Toner compositions of the invention which contain positive charge agents have provided the best transfer efficiency.

Although charge agents are generally incorporated in toner particles at concentrations of 0.5 to 5 weight percent, more commonly 1.0 to 1.5 percent, of the toner polymer, only that portion of the charge agent on the toner surface is effective. U.S. Pat. 4,756,991 discloses the surface coating of a fluorescent toner by a water-soluble polymeric quaternary ammonium compound at a level of at least 0.5 weight percent in combination with a liquid slip agent such as silicone oil. U.S. Pat. 4,224,396 also discloses the application of polymeric quaternary ammonium compounds, typically at a concentration of less than 1 percent by weight, to the surface of the toner. In Japanese Kokai 59135479, 0.2 to 5 weight percent of a cationic surfactant, which can be an alkylamine salt or a quaternary ammonium salt, is applied to the surface of colored toner particles from a polar solvent in which the toner has low solubility.

In some embodiments of the present invention, charge agents are conveniently and beneficially applied to toner particles simultaneously with the small, uniformly distributed surface particles by including the charge agents in the aqueous dispersions of the small particles. The charge agents can be soluble in water or in a mixture of water with another solvent, for example, methanol. Because the charge agents are also on the surface of the toner particles, they are effective at levels of 0.0025 to 0.1 percent, preferably 0.01 to 0.05 percent, based on the weight of toner polymer, which is much lower than the concentrations normally employed when the charge agents are melt-blended in the polymer.

Examples of suitable colorants are disclosed in U.S. Pat. Nos. 4,140,644; 4,416,965; 4,414,152; and 2,229,513. For black toners, carbon black is a preferred pigment.

The toner is crushed and ground to a desired particle size using, for example, fluid energy or a jet mill such as is described in U.S. Pat. 4,089,472.

Other procedures for the preparation of toner particles are also useful. For example, U.S. Pat. 4,833,060, discloses the preparation of small spherical particles by an evaporative limited coalescence process. Toner microbeads of very small particle size can be made by limited coalescence suspension polymerization as disclosed, for example, in U.S. Pat. 2,932,629. Dyes can be incorporated into the particles by adding them simultaneously with the formation of the polymers or subsequently thereto. Alternatively, a polymer solution in a solvent in combination with colorants and/or charge agents can be spray dried to form toner particles.

Commercial copying machines commonly employ toner particles in the size range of 10 µm to 30 µm in average diameter. Toner particles of smaller size are desirable for improving image resolution, but it is very difficult to transfer them electrostatically with a high degree of efficiency. An important advantage of the method of the invention is that it can produce small coated toner particles that are transferred very efficiently, even though the starting uncoated toners do not transfer well. In the practice of the present invention, toner particles in the average size range of 1 µm to 15 µm are preferred. Particularly preferred are toner particles of 2 µm to 6 µm average size. Average particle size as used herein refers to volume average, as measured by a Coulter Multisizer II® counter.

Coated toners prepared in accordance with the present invention from starting toner particles of the particularly preferred size range are especially useful for heat assisted electrostatic transfer, as disclosed in commonly-assigned copending U.S. Patent application of Aslam, et al., Serial No. 07/843,666, entitled "Image Forming Method and Apparatus Using an Intermediate" filed 28 February 1992.

The toner particles in accordance with the invention can be mixed with carrier particles to form a developer composition. The carrier particles can be selected from a variety of materials. Such materials include carrier core particles and core particles overcoated with a thin layer of resin that improves triboelectric charging of the toner particles. Examples of suitable resins are described in U.S. Pat Nos. 3,547,822; 3,632,512; 3,795,618; 3,898,170; 4,545,060; 4,478,925; 4,076,857; and 3,970,571.

The carrier core particles can comprise conductive, non-conductive, magnetic, or non-magnetic materials, examples of which are disclosed in U.S. Pat Nos. 3,850,663 and 3,970,571. Especially useful are porous iron particles having oxidized surfaces, steel particles, and ferromagnetic materials such as gamma ferric oxides or ferrites of barium, strontium, lead, magnesium, or aluminum; see, for example, U.S. Pat. Nos. 4,042,518; 4,478,925; and 4,546,060.

The surfaces of the toner particles in the thermally fixable toner compositions prepared in accordance with the invention are uniformly coated with small particles, which are coated from an aqueous dispersion. A surfactant such as Triton X-100® (from Rohm and Haas Co.) can optionally be added to this dispersion. These small particles can be either inorganic materials or organic polymers and can be applied to the toner particle surfaces at a concentration of from 0.1 to 10 weight percent of the toner particles. The small particles can have an average diameter of from 0.01 µm to 0.2 µm, preferably from 0.02 µm to 0.1 µm.

Inorganic materials suitable for the small coating particles include, for example, metal oxides such as SiO_2, Al_2O_3, and TiO_2. Silica is preferred. Aqueous colloidal dispersions of silica with average particle diameters of from 0.02 µm to 0.08 µm are especially preferred. The dispersions can be stabilized by sodium ions or ammonium ions, or they can be acid stabilized. Such materials are available from Nalco Chemical Company. Surfactants can be used to facilitate the application of the small particles from aqueous dispersions to the toner particles.

Organic polymers suitable for the small coating particles include homopolymers and copolymers of styrene or substituted styrenes, acrylic homopolymers and copolymers, and styrene-acrylic copolymers. Monodisperse latex dispersions with average particle size of from 0.02 µm to 0.2 µm are preferred.

In accordance with the method of the invention, the small particles are applied to the starting toner particles by mixing an aqueous dispersion thereof with the toner particles, with vigorous mechanical agitation. The slurry of coated toner particles is subsequently dried by heating either at atmospheric pressure or under vacuum, while continuing mechanical agitation of the mixture. The wet coated toner particles can be heated by apparatus such as a convection oven or a microwave oven. A preferred drying method in accordance with the invention is to heat the toner particles in a microwave oven which is at a low power level and is under vacuum. Alternatively, the wet coated toner particles can be spray dried by suspending them in a heated chamber until the water is evaporated, or they can be vacuum flash dried by heating with a heat exchanger prior to introduction into a vacuum chamber.

In some other embodiments of the present invention the toner particles are spray coated. In this procedure the uncoated toner particles are fluidized in a heated chamber by a gaseous stream while being sprayed by an aqueous dispersion of the small particles, after which the coated toner particles are allowed to dry in the heated chamber.

The invention is further illustrated in the following examples. Where toner charge in a developer is indicated, usually as microcoulombs per gram (µc/g), the charge was determined by a technique referred to as the "MECCA" method, wherein the apparatus consists of two parallel metal plates separated by insulating posts 1 cm high. An AC electromagnet is located beneath the lower plate to provide magnetic agitation, and a DC electric potential of about 2000 volts can be applied across the plates. For example, for a toner of 12 µm particle size, a developer is prepared by combining 12 parts of the toner with 88 parts of a suitable carrier. (For a toner of smaller particle size, a lower concentration of toner in the developer is used.) A weighed sample of 0.1 g of the developer is placed on the lower plate, and charged by magnetic agitation for 30 seconds. (In some of the examples, agitation was carried out for a period of 2 minutes.) Next, both the electric and magnetic fields are applied for 30 seconds. (In some of the examples, 2 minutes). The toner is separated from the carrier by the combined effect of the magnetic agitation and electric field and is transported to the upper plate of the apparatus by the electric field. The charge on the toner collected on the upper plate is measured in microcoulombs by an electrometer, and the weight of toner is determined. The charge per mass of toner is calculated by dividing the charge by the weight of transferred toner.

Example 1

To 40g of a black pigmented styrene-butyl acrylate toner (particle size, 8 µm, volume average) and 25 ml of water in a Sunbeam Mixmaster® mixer was added, dropwise, 6g of an aqueous dispersion of silica containing 5 weight percent solids. This dispersion was prepared by dilution of Nalcoag 1060® colloidal silica (from Nalco Chemical Company), a 50 weight percent dispersion of silica particles having an average size of 0.060 µm. After agitation for 30 minutes, the water was evaporated by heating in a microwave oven which was at a low power level and under vacuum, followed by air drying. The amount of silica on the coated toner was 0.75 parts/100 parts of the core toner particles, or approximately 0.75 weight percent.

By a similar procedure, toners containing 1.5, 2.0, and 2.5 weight percent coated silica were prepared.

Toner charge measurements were made on developers containing the silica-coated toners and the uncoated core particles by the above-described MECCA method. In addition, the toners of the invention were tested for their gap-jumping transfer performance by affixing paper reinforcement rings (inner diameter 6 mm, outer diameter 14 mm and of 75 µm thickness) to receiver paper and transferring patches of toned images from a photoconducting film to the receiver, using roller transfer. The receiver areas within the rings were typically in poorer contact with the photoconducting film than the areas outside them, causing lower transfer densities inside the rings than outside. Densities within the rings expressed as percentages of densities outside the rings provide a measure of efficiency and image quality. The results of these test were as follows:

Test	Weight Percent Coated Silica	MECCA Charge (µc/g)	Percent Transfer Inside Ring
1	0	72	44
2	0.75	46	69
3	1.5	32	84
4	2.0	28	92
5	2.5	24	95

Compared with the uncoated toner, the charge on silica-coated toners of the invention was significantly lowered, the higher the silica concentration the lower the charge. In addition, the density of the transferred images inside the reinforcement rings markedly increased with increasing amounts of silica coated on the toner particles. These results demonstrate the superior charge properties and imaging performance of toner compositions of the invention.

Example 2

By the procedure described in Example 1, a mixture of 40g of the toner and 53 ml of water was treated with 4g of an aqueous dispersion of aluminum oxide containing 5 weight percent solids. This dispersion was prepared from Aluminum Oxid C®, from Degussa Corp. After thorough mixing, the coated toner was dried. The amount of aluminum oxide on this toner was 0.5 parts/100 parts of the core toner particles, or approximately 0.5 weight percent.

By a similar procedure, toners containing 1.0, 1.5, and 2.0 weight percent coated aluminum oxide were prepared.

Toner charge measurements were made on developers containing the aluminum oxide-coated particles and the uncoated core particles by the above-described MECCA method. Gap-jumping transfer performance was also evaluated by the procedure described in Example 1. The results of these tests follow:

Test	Weight Percent Coated Aluminum Oxide	MECCA Charge (μc/g)	Percent Transfer Inside Ring
1	0	72	44
2	0.5	39	77
3	1.0	37	84
4	1.5	33	94
5	2.0	29	98

Compared with the uncoated toner, the charge on aluminum oxide-coated toners of the invention was significantly decreased, the higher the concentration of aluminum oxide the lower the charge. In addition, the percentage of toner transferred inside the reinforcement rings was greatly increased for the alumina-coated toners.

Example 3

To 50g of a cyan polyester (Kodak Coloredge®) toner containing 4.0 weight percent of a bridged aluminum phthalocyanine pigment (prepared as described in U.S. Pat. 4,311,775) and having a particle size of 12.7 μm (volume average) in a Waring blender was added dropwise 12.5g of an aqueous dispersion of silica containing 4 weight percent solids. This dispersion was prepared by dilution of Nalcoag 1060® colloidal silica, described in Example 1. After the addition of the dispersion, the mixture was agitated for 30 minutes longer, then transferred to a large dish. The amount of silica on the coated toner was 1.0 part/100 parts of the core toner particles, or approximately 1.0 weight percent.

Using the procedure described above for the cyan toner, 50g of a yellow polyester (Kodak Coloredge®) toner containing 3.0 weight percent Novoperm yellow pigment (from Hoechst Co.) and having a particle size of 15.3 μm (volume average) was mixed with 12.5g of an aqueous dispersion of silica prepared from Nalcoag 1060® colloidal silica, containing 4 weight percent solids. The amount of silica on the coated yellow toner was 1.0 part/100 parts of the core toner particles, or approximately 1.0 weight percent.

Similarly, 50g of a magenta polyester (Kodak Coloredge®) toner containing 2.0 weight percent of a Rhodamine dye and having a particle size of 12.1 μm (volume average) was treated with 12.5g of an aqueous dispersion of silica prepared from Nalcoag 1060® colloidal silica, containing 4 weight percent solids. The amount of silica on the coated magenta toner was 1.0 part/100 parts of the core toner particles, or approximately 1.0 weight percent.

Toner charge measurements were made on developers containing the silica-coated toners and the uncoated core particles by the above-described MECCA method. Gap-jumping transfer performance was also evaluated as described in Example 1. The results of these measurements were as follows:

Test	Toner	Weight Percent Coated Silica	MECCA Charge (μc/g)	Percent Transfer Inside Ring
1	cyan	0	38.2	72
2	"	1.0	11.9	92
3	yellow	0	29.6	57
4	"	1.0	13.4	90
5	magenta	0	54.2	62
6	"	1.0	15.4	93

These results illustrate the large reduction in charge and the great improvement in gap-jumping transfer performance produced by coating cyan, yellow, and magenta toners with small particles of silica, in accordance with the present invention.

Example 4

Using the procedure of Example 1, a mixture of 40g of cyan polyester toner having a particle size of 9 μm (volume average) and 46 ml water was treated with 4g of an aqueous dispersion of silica, prepared from Nalcoag 1060® colloidal silica, and containing 5 weight percent solids and 0.3% Triton X-100® surfactant (a nonionic polyether detergent from Rohm and Haas Co.). The coated toner particles, which were dried in a microwave oven at low power and under vacuum, contained 0.5 parts silica/100 parts of the core toner particles, or approximately 0.5 weight percent.

By a similar procedure, toners containing 1.0, 2.0, and 3.0 weight percent coated silica were prepared.

Toner charge was measured for developers containing the silica-coated toner particles by the above-described MECCA method. The results follow:

Test	Weight Percent Coated Silica	MECCA Charge (μc/g)
1	0.5	60.9
2	1.0	41.7
3	2.0	32.6
4	3.0	27.2

These data illustrate the continuing decrease in toner charge with increasing amount of silica coated in accordance with the method of the invention.

Example 5

Toner particles with an average diameter of 3.5 μm and containing 200 parts Piccotoner 1221®, a styrene-butyl acrylate copolymer from Hercules Co., 32 parts of bridged aluminum phthalocyanine pigment, and 0.3 parts of octadecyldimethyl-benzylammonium m-nitrobenzenesulfonate as charge agent were prepared and washed, using the evaporative limited coalescence process disclosed in U.S. Pat. 4,833,060. A 40g portion of these particles was mixed with 32 ml water and 8g of an aqueous dispersion of silica containing 5 weight percent solids, using the procedure described in Example 1. The aqueous dispersion was prepared by dilution of Nalcoag 1050® colloidal silica, a 50 weight percent dispersion of silica particles having an average size of 0.020 μm. The amount of silica on the coated cyan toner, which was dried as described in Example 1, contained 1.0 parts/100 parts of the core toner particles, or approximately 1.0 weight percent.

By a similar procedure, toners containing 1.5 and 2.0 weight percent coated silica were prepared.

Measurements of toner charge were made on developers containing the silica-coated toners and the uncoated core particles by the above-described MECCA method. The results follow:

Test	Weight Percent Coated Silica	MECCA Charge (μc/g)
1	0	327
2	1.0	161
3	1.5	146
4	2.0	98

These results illustrate the progressive reduction in toner charge produced by increasing amounts of very small silica particles, coated on the toner in accordance with the method of the invention.

Example 6

A 40g portion of the small cyan toner particles prepared as described in Example 5 was mixed in a Waring blender as described in Example 3 with 29.2g of an aqueous dispersion of silica containing 5 weight percent solids, which dispersion was prepared by dilution of Nalcoag 1060® colloidal silica. The silica-coated toner particles, which were dried at room temperature, contained 3.0 parts silica/100 parts of the core toner particles, or about 3.0 weight percent.

Another 40g portion of the cyan toner particles described in Example 5 was treated in a Sunbeam Mixmaster® mixer with a mixture of 7 ml water and 50g of a monodisperse latex of a styrene-sodium styrenesulfonate copolymer containing 2.4 weight percent solids and having an average particle size of 0.1 μm. After agitation to ensure uniform coating of the toner, the particles were dried under vacuum in a microwave oven at 30% power. The amount of styrene copolymer on the coated toner was 3.0 parts/100 parts of the core toner particles, or about 3.0 weight percent.

A third 40g portion of the toner particles described in Example 5 was treated in a Sunbeam Mixmaster® mixer with a mixture of 16 ml water and 24g of an aqueous dispersion of aluminum oxide containing 5 weight percent solids, which had been prepared from Aluminum Oxid C®, from Degussa Corp. The particles were dried under vacuum in a microwave oven at 30% power. The amount of aluminum oxide on the coated toner was 3.0 parts/100 parts of the core toner particles, or about 3.0 weight percent.

The cyan toner particles coated as described above with aqueous dispersions of silica, polymer beads, and aluminum oxide were tested with the apparatus described in the copending Aslam, et al., application cited above. An aluminum drum was covered first with a 33-ml thick polycarbonate sheet of 87 Shore A hardness and then with an inverse composite organic photoconductor element. The photoconductive layers were charged to + 450 volts and exposed for 2 seconds through a 0.7 neutral density filter. The discharged areas of the photoconductor were toned with a magnetic brush at a bias of 45 volts with the three coated toners and the starting uncoated toner described above, all positively charged. The cyan toner images so formed were transferred to a nickel intermediate sheet wrapped around a metallic drum. An electrical field of 450 volts was created by biasing the metallic transfer drum and grounding the conductive layer of the photoconductive element. The cyan images were transferred from the intermediate to a receiver sheet at temperatures from 70° to 90° C and linear pressures of 3.6 or 5.4 kg per linear cm (20 or 30 pounds per linear inch).

The percentage of toner transfer was determined by transferring the image that had been transferred to the intermediate and the residual image on the photoconductor to separate receiver sheets. The reflection densities of the images on each of the receiving sheets were measured by a densitometer and used to calculate the percent transfer.

The following results were obtained from these tests:

Test	Small Particles on Toner	Transfer Temperature(°C)	Transfer Pressure (kd/linear cm)	Percent Transfer
1	None	90	5.4	97
2	SiO_2	90	5.4	99
3	None	70	3.6	83
4	None	80	3.6	84
5	None	90	3.6	84
6	SiO_2	70	3.6	99
7	SiO_2	80	3.6	99
8	SiO_2	90	3.6	99
9	Copolymer	70	3.6	97
10	Copolymer	80	3.6	98
11	Copolymer	90	3.6	98
12	Al_2O_3	70	3.6	95
13	Al_2O_3	80	3.6	94
14	Al_2O_3	90	3.6	95

The above results demonstrate the outstanding transfer performance over a range of temperatures and pressures of 3.5 µm cyan toner particles coated with an aqueous dispersion of silica in accordance with the method of the invention. Excellent transfer results were also obtained with the toner coated with particles of styrene-sodium styrenesulfonate copolymer. Similarly, the aluminum oxide-coated toner yielded much higher transfer percentages than the uncoated toner.

Example 7

A black pigmented styrene-butyl acrylate toner containing no incorporated charge control agent was treated as in Example 1 with aqueous dispersions that were prepared by diluting Nalcoag 1060® colloidal silica from its starting 50 weight percent of silica particles to 1.5 percent and adding the water-soluble charge agent lauramidopropyltrimethylammonium methylsulfate at concentrations of 0.005 to 0.05 percent. The coated toner particles obtained after agitation and drying contained 1.5 weight percent silica and 0.005 to 0.5 weight percent charge agent on their surfaces. As a control, 1 weight percent of the same quaternary ammonium charge agent was melt-compounded into the above described toner, which was then surface coated with 1.5 weight percent silica from an aqueous dispersion that contained no charge agent.

Toner charge measurements were made on developers containing the silica- and charge agent-coated toner particles and the control toner by the MECCA method described above, using an agitation time of 2 minutes. The results of these tests were as follows:

Test	Weight Percent Coated Silica	Weight Percent Coated Charge Agent	MECCA Charge (µc/g) 2 minutes agitation
1 (Control)	1.5	0	8.3
2	1.5	0.005	11.2
3	1.5	0.015	9.3
4	1.5	0.05	10.6

As the above data show, the MECCA charging performance of a toner coated with silica and as little as 0.005 weight percent of charge agent on the surface was comparable to a silica-coated toner containing 1 weight percent of the same charge agent compounded in the polymer melt.

Fusing characteristics of toner compositions of the invention, that is, the ability of toner images deposited on paper to resist removal when the paper is creased and rubbed, were improved as the level of charge agent coated on the surface of the toner particles was increased from 0.005 to 0.05 weight percent. The performance of the toner surface-coated with 1.5 percent silica and 0.05 percent charge agent was similar to that containing no coated silica and 1 percent of melt-compounded charge agent at fusing temperatures in the range of 177-218 °C.

Example 8

The toner containing no incorporated charge control agent of Example 7 was treated with a dilute aqueous dispersion that was prepared from Nalcoag 1060® colloidal silica and contained 1.0 percent silica and 0.0025 to 0.25 percent of the charge agent N-(2-benzoyloxyethyl)-N,N-dimethylbenzylammonium m-nitrobenzenesulfonate. This latter compound was not water-soluble but did remain dissolved when added from a 10 percent methanol solution to the aqueous silica dispersion.

The coated toner particles were dried and formulated into developers, whose charge performance was measured as in Example 7. The results were as follows:

Test	Weight Percent Coated Silica	Weight Percent Coated Charge Agent	MECCA Charge (µc/g) 2 minutes agitation
1 (Ex. 7 Control)	1.5	0	8.3
2	1.0	0.0025	9.8
3	1.0	0.010	11.6
4	1.0	0.025	16.0

The above data illustrate the good MECCA charge performance of toner compositions of the present invention, even with a concentration of charge agent on the toner particle surface as low as 0.0025 weight percent.

Claims

1. A thermally fixable electrostatographic toner composition comprising thermoplastic toner particles, characterized in that the toner particles have aqueous-dispersible small particles strongly adhered upon their surfaces in a uniform distribution, and the small particles have an average diameter from 0.01 µm to 0.2 µm.

2. The toner composition of Claim 1, wherein the small particles have been adhered to the toner particles by mixing an aqueous dispersion of the small particles with the toner particles, agitating the resulting mixture to ensure uniform distribution, and drying the toner particles.

3. The toner composition of Claim 2, wherein the aqueous dispersion contains a charge agent.

4. The toner composition of Claim 1, wherein the toner particles comprise a thermoplastic cross-linked binder resin and a colorant uniformly dispersed therein.

5. The toner composition of Claim 1, wherein the toner particles have a charge agent on their surfaces and the concentration of the charge agent is from 0.0025 to 0.1 weight percent of the toner particles.

6. The toner composition of Claim 1, wherein the small particles are colloidal silica, aluminum oxide, or a latex polymer.

7. The toner composition of Claim 1, wherein the amount of the small particles is from 0.1 to 10 weight percent of the toner particles.

8. The toner composition of Claim 1, wherein the toner particles have an average diameter from 1 μm to 15 μm.

9. The toner composition of Claim 1, wherein the small particles have an average diameter from 0.02 μm to 0.08 μm.

10. The toner composition of Claim 2, wherein the mixing has been carried out by spraying the dispersion on the toner particles while fluidizing the toner particles in a gaseous stream.

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EUROPEAN SEARCH REPORT

Application Number

EP 93 10 3079

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X Y	EP-A-0 197 242 (TORAY INDUSTRIES, INC.) * page 4, line 3 - line 7 * * page 14, line 5 - page 18, line 13; example 8 * ---	1,2,6-9 4,5	G03G9/097
Y A	EP-A-0 365 344 (MITA INDUSTRIAL CO., LTD.) * page 4, line 20 - page 5, line 20; claim 1 * ---	4 3,5	
P,Y	DATABASE WPIL Week 9244, Derwent Publications Ltd., London, GB; AN 92-360234 & JP-A-4 260 059 (HITACHI METALS LTD.) 16 September 1992 * abstract * ---	4,5	
A	DE-A-3 208 635 (CANON K.K.) * claims 1-7; example 1 * ---	1-9	
A	GB-A-2 133 571 (CANON KABUSHIKI KAISHA) * page 4, line 35 - line 55; examples 1-3 * ---	1-9	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
A	PATENT ABSTRACTS OF JAPAN vol. 5, no. 201 (P-94)(873) 19 December 1981 & JP-A-56 121 050 (CANON K.K.) 22 September 1981 * abstract * ---	1-9	G03G
A	PATENT ABSTRACTS OF JAPAN vol. 5, no. 202 (P-95)22 December 1981 & JP-A-56 123 550 (HITACHI METALS LTD.) 28 September 1981 * abstract * -----	1-10	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	07 JUNE 1993	HINDIAS E.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
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