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Improved toner and process for forming two-color images.

Disclosed is a toner composition comprising a resin, a colorant, and a charge control additive selected from the group consisting of (a) zinc 3,5-di-tert-butyl salicylate compounds; (b) mixtures of a zinc 3,5-di-tert-butyl salicylate compound and an alkyl pyridinium halide; (c) mixtures of a zinc 3,5-di-tert-butyl salicylate compound and distearyl dimethyl ammonium methyl sulfate; (d) mixtures of a zinc 3,5-di-tert-butyl salicylate compound and distearyl dimethyl ammonium bisulfate; (e) mixtures of an aluminum 3,5-di-tert-butyl salicylate compound and an alkyl pyridinium halide; (f) mixtures of an aluminum 3,5-di-tert-butyl salicylate compound and distearyl dimethyl ammonium methyl sulfate; (g) mixtures of an aluminum 3,5-di-tert-butyl salicylate compound and distearyl dimethyl ammonium bisulfate; and mixtures thereof, a colloidal silica external additive, and a metal salt of a fatty acid external additive. Also disclosed are imaging processes employing the toner, including a process for forming two-color images which comprises creating on an imaging member a latent image comprising areas of high, medium, and low potential, developing the low areas of potential with a developer comprising the toner disclosed herein and a carrier, subsequently developing the high areas of potential with a developer comprising a toner of a second color and a carrier, transferring the developed two-color image to a substrate, and optionally permanently affixing the image to the substrate.

The present invention is directed to improved toner compositions and to an improved process for forming two-color images.

US-A-4,845,003 discloses a toner for developing electrostatic latent images characterized in that the toner comprises an aluminum compound of a hydroxycarboxylic acid which may be substituted with alkyl and/or aralkyl.

US-A-4,656,112 discloses a toner for developing electrostatic latent images which is characterized in that the toner comprises as a charge control agent a zinc complex compound of an aromatic hydroxycarboxylic acid having or not having a substituent.

Other disclosures of background interest are to be found in US-A-4,314,017, US-A-4,604,338, US-A-4,206,064, US-A-4,902,598, US-A-4,824,750, and US-A-4,904,762.

The process of charging a photoresponsive imaging member to a single polarity and creating on it an image consisting of at least three different levels of potential of the same polarity is disclosed in US-A-4,078,929. This patent discloses a method of creating two colored images by creating 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. According to the teachings of this patent, however, the images produced are of inferior quality compared to those developed in two successive development steps. Also of interest with respect to the tri-level process for generating images is US-A-4,686,163.

US-A-4,525,447 and US-A-4,640,883 also disclose methods of forming composite or dichromatic images which comprises forming on an imaging member electrostatic latent images having at least three different potential levels.

US-A-4,948,686 discloses 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 with a developer comprising a colored first toner comprising a first resin selected from the group consisting of polyesters, styrene-butadiene polymers, styrene-acrylate polymers, styrene-methacrylate polymers, and mixtures thereof; a first pigment; a charge control agent; colloidal silica surface external additives present; and external additives comprising metal salts or metal salts of fatty

acids; and a first carrier comprising a core 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 polymethylmethacrylate 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; (4) subsequently developing the high areas of potential with a developer comprising a black second toner comprising a second resin present selected from the group consisting of polyesters, styrene-butadiene polymers, styrene-acrylate polymers, styrenemethacrylate polymers, and mixtures thereof; a second pigment; and a second charge control additive; and a second carrier comprising a core 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; polyvinylfluoride; and polyvinylchloride; and (5) transferring the developed two-color image to a substrate.

Although known compositions and processes are suitable for their intended purposes, a need remains for toners, developers, and imaging processes that enable generation of high quality two-color images in a single development pass, particularly as a result of the absence of interaction between the black and color developers. A need also remains for toners, developers, and imaging processes that enable reduction or elimination of fringe-field development (the development of a halo of one color toner surrounding an image developed with the other color toner). There is also a need for toner compositions that enable improved developer conductivity. Further, there is a need for toner compositions that enable improved developer admix properties (the amount of time required for new toner particles added to the mixture of toner particles and carrier particles to acquire the desired triboelectric charge).

It is an object of the present invention to provide toners, developers, and imaging processes that enable generation of high quality two-color images in a single development pass.

According to one aspect of the invention, there is provided a toner composition comprising a resin, a colorant, a charge control additive, comprising a mixture of (a) at least one first material selected from aluminum 3,5-di-tert-butyl salicylate compounds and zinc 3,5-di-tert-butyl salicylate compounds, and (b) at least one second material selected from alkyl pyridinium halides, distearyl dimethyl ammonium methyl sulfate, and distearyl dimethyl ammonium bisulfate, a colloidal silica external additive, and a metal salt of a fatty acid external additive.

The invention provides a process for forming two-color images which comprises charging an imaging member, creating on the member a latent image

comprising areas of high, medium, and low potential, developing the low areas of potential with a developer comprises a toner of a first color comprising a resin, a colorant, a charge control additive selected from the group consisting of (a) zinc 3,5-di-tert-butyl salicylate compounds; (b) mixtures of a zinc 3,5-di-tert-butyl salicylate compound and an alkyl pyridinium halide; (c) mixtures of a zinc 3,5-di-tert-butyl salicylate compound and distearyl dimethyl ammonium methyl sulfate; (d) mixtures of a zinc 3,5-di-tert-butyl salicylate compound and distearyl dimethyl ammonium bisulfate; (e) mixtures of an aluminum 3,5-di-tert-butyl salicylate compound and an alkyl pyridinium halide; (f) mixtures of an aluminum 3,5-di-tert-butyl salicylate compound and distearyl dimethyl ammonium methyl sulfate; (g) mixtures of an aluminum 3,5-di-tert-butyl salicylate compound and distearyl dimethyl ammonium bisulfate; and mixtures thereof, a colloidal silica external additive, and a metal salt of a fatty acid external additive, and a carrier, subsequently developing the high areas of potential with a developer comprising a toner of a second color and a carrier, transferring the developed two-color image to a substrate, and optionally permanently affixing the image to the substrate. Another embodiment of the present invention is directed to a process for forming two-color images which comprises (1) creating on an imaging member in an imaging apparatus a latent image comprising areas of high, intermediate, and low potential; (2) developing the low areas of potential by conductive magnetic brush development with a developer comprising a first toner of a first color 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, styrene-acrylate 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, substituted copper phthalocyanine pigments, halogenated phthalocyanine pigments, quinacridone pigments, azo pigments, rhodamine pigments, and mixtures thereof; a charge control agent present in an amount of from about 0.1 to about 5 percent by weight and selected from the group consisting of (a) zinc 3,5-di-tert-butyl salicylate compounds; (b) mixtures of a zinc 3,5-di-tert-butyl salicylate compound and an alkyl pyridinium halide; (c) mixtures of a zinc 3,5-di-tert-butyl salicylate compound and distearyl dimethyl ammonium methyl sulfate; (d) mixtures of a zinc 3,5-di-tert-butyl salicylate compound and distearyl dimethyl ammonium bisulfate; (e) mixtures of an aluminum 3,5-di-tert-butyl salicylate compound and an alkyl pyridinium halide; (f) mixtures of an aluminum 3,5-di-tert-butyl salicylate compound and distearyl dimethyl ammonium methyl sulfate; (g) mixtures of an aluminum 3,5-di-tert-butyl salicylate compound and distearyl dimethyl

ammonium bisulfate; and mixtures thereof; 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 polymethylmethacrylate 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; (3) subsequently developing the high areas of potential by conductive magnetic brush development with a developer comprising a second toner of a second color 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 (4) transferring the developed two-color image to a substrate. Still another embodiment of the present invention is directed to an imaging process which comprises forming an electrostatic latent image on an imaging member, developing the latent image with a toner composition comprising a resin, a colorant, a charge control additive selected from the group consisting of (a) mixtures of a zinc 3,5-di-tert-butyl salicylate compound and an alkyl pyridinium halide; (b) mixtures of a zinc 3,5-di-tert-butyl salicylate compound and distearyl dimethyl ammonium methyl sulfate; (c) mixtures of a zinc 3,5-di-tert-butyl salicylate compound and distearyl dimethyl ammonium bisulfate; (d) mixtures of an aluminum 3,5-di-tert-butyl salicylate compound and an alkyl pyridinium halide; (e) mixtures of an aluminum 3,5-di-tert-butyl salicylate compound and distearyl dimethyl ammonium methyl sulfate; (f) mixtures of an aluminum 3,5-di-tert-butyl salicylate compound and distearyl dimethyl

ammonium bisulfate; and mixtures thereof, a colloidal silica external additive, and a metal salt of a fatty acid external additive, transferring the developed image to a substrate, and optionally permanently affixing the transferred image to the substrate.

Toners of the present invention generally comprise a resin or resins, one or more pigments, a charge control agent selected from the group consisting of (a) zinc 3,5-di-tert-butyl salicylate compounds; (b) mixtures of a zinc 3,5-di-tert-butyl salicylate compound and an alkyl pyridinium halide; (c) mixtures of a zinc 3,5-di-tert-butyl salicylate compound and distearyl dimethyl ammonium methyl sulfate; (d) mixtures of a zinc 3,5-di-tert-butyl salicylate compound and distearyl dimethyl ammonium bisulfate; (e) mixtures of an aluminum 3,5-di-tert-butyl salicylate compound and an alkyl pyridinium halide; (f) mixtures of an aluminum 3,5-di-tert-butyl salicylate compound and distearyl dimethyl ammonium methyl sulfate; (g) mixtures of an aluminum 3,5-di-tert-butyl salicylate compound and distearyl dimethyl ammonium bisulfate; and mixtures thereof, a colloidal silica external additive, and a metal salt of a fatty acid external additive. Suitable resins include polyesters and 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, preferably about 88 percent by weight, and the butadiene portion is present in an amount of from about 7 to about 17 percent by weight, preferably about 12 percent by weight, such as the resins commercially available as Pliolite® or Pliotone® from Goodyear. Also suitable are styrene acrylate polymers and styrene-n-butylmethacrylate polymers, particularly those styrene-n-butylmethacrylate copolymers wherein the styrene portion 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 portion 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 are also suitable. Also particularly suitable for inclusion in the toners for the present invention are styrene-n-butylmethacrylate polymers wherein the styrene portion is present in an amount of from about 50 to about 80 percent by weight, preferably about 65 percent by weight, and the n-butylmethacrylate portion is present in an amount of from about 50 to about 20 percent by weight, preferably about 35 percent by weight. The resin is generally present in an amount of from about 80 to about 98.8 percent by weight.

Suitable toner pigments include copper phthalocyanine pigments, substituted copper phthalocyanine pigments, halogenated phthalocyanine pigments, quinacridone pigments, azo pigments, rhodamine pigments, and mixtures thereof. Specific examples include Fanal Pink, commercially available from

BASF, Sudan Blue OS, commercially available from BASF, Neopen Blue, commercially available from BASF, PV Fast Blue, commercially available from Hoechst-Celanese, Lithol Scarlet, commercially available from BASF, Heliogen Green K-9360, commercially available from BASF, Hostaperm Pink E pigment, commercially available from Hoechst-Celanese, Fanchon Fast Red R-6226, commercially available from Mobay Chemical Company, Permanent Yellow FGL, commercially available from Hoechst-Celanese, monoazo pigments such as Pigment Red 48:1, and the like. Generally, the pigment is present in an amount of from about 1 to about 15 percent by weight, and preferably from about 2 to about 10 percent by weight.

Suitable charge control agents for the toners of the present invention include zinc 3,5-di-tert-butyl salicylate compounds, such as Bontron E-84, available from Orient Chemical Company of Japan, or zinc compounds as disclosed in US-A- 4,656,112, mixtures of a zinc 3,5-di-tert-butyl salicylate compound with a second charge control agent such as alkyl pyridinium halides, including cetyl pyridinium chloride and others as disclosed in US-A- 4,298,672, distearyl dimethyl ammonium methyl sulfate as disclosed in US-A-4,560,635, and distearyl dimethyl ammonium bisulfate as disclosed in US-A-4,937,157, and US-A-4,560,635, mixtures of an aluminum 3,5-di-tert-butyl salicylate compound, such as Bontron E-88, available from Orient Chemical Company of Japan, or aluminum compounds as disclosed in US-A-4,845,003, with a second charge control agent such as alkyl pyridinium halides, including cetyl pyridinium chloride and others, distearyl dimethyl ammonium methyl sulfate, and distearyl dimethyl ammonium bisulfate; and mixtures thereof.

The zinc compound charge control additives are compounds of zinc with 3,5-ditertiary-butyl salicylic acid as disclosed in US-A- 4,656,112.

The aluminum compound charge control additives are compounds of aluminum with 3,5-di-tertiary-butyl salicylic acid, and according to US-A-4,845,003 are prepared from an aromatic hydroxycarboxylic acid with an alkyl and/or aralkyl by treating the acid with an aluminum imparting agent by a known method.

The charge control agent or mixture of charge control agents is generally present in a total amount of from about 0.1 to about 10 percent by weight, and preferably from about 0.25 to about 3 percent by weight, although other amounts may be present provided that the objectives of the present invention are achieved. In one preferred embodiment, the charge control agent is a mixture of either a zinc compound of 3,5-di-tert-butyl salicylate or an aluminum compound of 3,5-di-tert-butyl salicylate with one of the second charge control agents, wherein the second charge control agent is present in the toner in an

amount of from about 0.1 percent by weight to about 1 percent by weight, and preferably from about 0.25 percent by weight to about 0.75 percent by weight.

In addition, external additives of colloidal silica, such as Aerosil® R972, Aerosil® R976, Aerosil® R812, and the like, available from Degussa, and metal salts or metal salts of fatty acids, such as zinc stearate, magnesium stearate, aluminum stearate, cadmium stearate, and the like, are blended on the surface of the toners of the present invention. In general, toners with these additives blended on the surface are disclosed in US-A-3,590,000, US-A-3,720,617, US-A-3,900,588, and US-A-3,983,045. Generally, the silica is present in an amount of from about 0.1 to about 2 percent by weight, and preferably about 0.3 percent by weight, of the toner and the metal salt additive such as zinc stearate is present in an amount of from about 0.1 to about 2 percent by weight, and preferably about 0.3 percent by weight, of the toner. Varying the amounts of these two external additives enables adjustment of the charge levels and conductivities of the toners. For example, increasing the amount of silica generally adjusts the triboelectric charge in a negative direction and improves admix times, which are a measure of the amount of time required for fresh toner to become triboelectrically charged after coming into contact with the carrier. In addition, increasing the amount of zinc stearate improves admix times, renders the developer composition more conductive, adjusts the triboelectric charge in a positive direction, and improves humidity insensitivity.

One particularly preferred embodiment of the present invention is directed to a toner comprising 90 percent by weight of a styrene-butadiene resin, such as Pliolite®, 7 percent by weight of a pigment, such as PV Fast Blue B2G-A, and 3 percent by weight of a zinc 3,5-di-tert-butyl salicylate compound, such as Bontron E-84, with external additives colloidal silica, such as Aerosil® R-972, present in an amount of about 0.3 percent by weight of the toner, and metal salts of fatty acids, such as zinc stearate, present in an amount of about 0.3 percent by weight of the toner. Another particularly preferred embodiment of the present invention is directed to a toner comprising 90.5 percent by weight of a styrene-butadiene resin, such as Pliolite®, 7 percent by weight of a pigment, such as PV Fast Blue, 2 percent by weight of a zinc 3,5-di-tert-butyl salicylate compound, such as Bontron E-84, and 0.5 percent by weight of an alkyl pyridinium halide, such as cetyl pyridinium chloride, with external additives colloidal silica, such as Aerosil® R-972, present in an amount of about 0.3 percent by weight of the toner, and metal salts of fatty acids, such as zinc stearate, present in an amount of about 0.3 percent by weight of the toner. Yet another particularly preferred embodiment of the present invention is directed to a toner comprising 90.5 percent by weight

of a styrene-butadiene resin, such as Pliolite®, 7 percent by weight of a pigment, such as PV Fast Blue, 2 percent by weight of an aluminum 3,5-di-tert-butyl salicylate compound, such as Bontron E-88, and 0.5 percent by weight of an alkyl pyridinium halide, such as cetyl pyridinium chloride, with external additives colloidal silica, such as Aerosil® R-972, present in an amount of about 0.3 percent by weight of the toner, and metal salts of fatty acids, such as zinc stearate, present in an amount of about 0.3 percent by weight of the toner.

Colored developers suitable for the imaging processes of the present invention comprise a toner of the present invention and a carrier. Any suitable electrophotographic carrier can be used. When the developer is used to develop two-color images according to the process of the present invention, preferred carriers are generally conductive, and generally exhibit a conductivity of, for example, from about 10^{-14} to about 10^{-6} (ohm-cm) $^{-1}$, and preferably from about 10^{-11} to about 10^{-7} (ohm-cm) $^{-1}$. Conductivity is generally controlled by the choice of carrier core and coating; by partially coating the carrier core, or by coating the core with a coating of a material containing carbon black, the carrier is rendered conductive. In addition, irregularly shaped carrier particle surfaces and toner concentrations of from about 0.2 to about 5 will generally render a developer conductive. Addition of a surface additive such as zinc stearate to the surface of the toner particles also renders a developer conductive with the level of conductivity rising with increased concentrations of the additive. Preferred carriers for the developers of the present invention generally comprise a steel core, preferably unoxidized, such as Hoeganoes Anchor Steel Grit, with an average diameter of from about 25 to about 215 microns, preferably from 50 to 150 microns, available from Hoeganoes, Riverton, NJ, or Toniolo non-round steel with an average diameter of from about 25 to about 215 microns, preferably from 50 to 150 microns, available from Pometom S.P.A. (Toniolo), Venezia, Italy. The carrier particles are coated with a solution coating of methyl terpolymer containing from 0 to about 40 percent by weight of conductive particles such as carbon black or other conductive particles as disclosed in US-A-3,533,835, homogeneously dispersed in the coating material with the coating weight being from about 0.2 to about 3 percent by weight of the carrier, and preferably from about 0.4 to about 1.5 percent by weight of the carrier. Alternatively, the carrier coating may comprise polymethylmethacrylate containing conductive particles in an amount of from 0 to about 40 percent by weight of the polymethylmethacrylate, and preferably from about 10 to about 20 percent by weight of the polymethylmethacrylate, wherein the coating weight is from about 0.2 to about 3 percent by weight of the carrier and preferably about 1 percent by weight of the carrier. A third pos-

sible carrier coating for the carrier of the developer comprises a blend of from about 35 to about 65 percent by weight of polymethylmethacrylate and from about 35 to about 65 percent by weight of chlorotrifluoroethylene-vinyl chloride copolymer, commercially available as OXY 461 from Occidental Petroleum Company containing conductive particles in an amount of from 0 to about 40 percent by weight, and preferably from about 20 to about 30 percent by weight, wherein the coating weight is from about 0.2 to about 3 percent by weight of the carrier, and preferably about 1 percent by weight of the carrier. Preferably, the carrier coatings are placed on the carrier cores by a solution coating process.

Colored developer compositions of the present invention prepared from this toner and carrier generally comprise from about 0.5 to about 5 percent by weight of the toner and from about 95 to about 99.5 percent by weight of the carrier. The ratio of toner to carrier may vary, however, provided that the objectives of the present invention are achieved. For example, an imaging apparatus employed for the process of the present invention may be replenished with a colored developer comprising about 55 percent by weight toner and about 45 percent by weight carrier. The triboelectric charge of the colored toners generally is from about -10 to about -30, and preferably from about -15 to about -20 microcoulombs per gram, although the value may be outside of this range provided that the objectives of the present invention are achieved. Particle size of the colored toners is generally from about 7 to about 20 microns in volume average diameter, and preferably about 13 microns in volume average diameter, although the value may be outside of this range provided that the objectives of the present invention are achieved.

The color developers of the present invention are particularly suitable for two-color imaging processes wherein a latent image comprising areas of high, medium, and low potential is developed with two different color developers. Imaging members suitable for use with the process of the present invention may be of any type capable of maintaining three distinct levels of potential. Generally, various dielectric or photoconductive insulating material suitable for use in xerographic, ionographic, or other electrophotographic processes may be used, and suitable photoreceptor materials include amorphous silicon, layered organic materials as disclosed in US-A-4,265,990.

The photoresponsive imaging member can be negatively charged, positively charged, or both, and the latent image formed on the surface may consist of either a positive or a negative potential, or both. In one embodiment, the image consists of three distinct levels of potential, all being of the same polarity. The levels of potential should be well differentiated, such that they are separated by at least 100 volts, and preferably 200 volts or more. For example, a latent image

on an imaging member can consist of areas of potential at -800, -400, and -100 volts. In addition, the levels of potential may consist of ranges of potential. For example, a latent image may consist of a high level of potential ranging from about -500 to about -800 volts, an intermediate level of potential of about -400 volts, and a low level ranging from about -100 to about -300 volts. An image having levels of potential that range over a broad area may be created such that gray areas of one color are developed in the high range and gray areas of another color are developed in the low range with 100 volts of potential separating the high and low ranges and constituting the intermediate, undeveloped range. In this situation, from 0 to about 100 volts may separate the high level of potential from the intermediate level of potential, and from 0 to about 100 volts may separate the intermediate level of potential from the low level of potential. When a layered organic photoreceptor is employed, preferred potential ranges are from about -700 to about -850 volts for the high level of potential, from about -350 to about -450 volts for the intermediate level of potential, and from about -100 to about -180 volts for the low level of potential. These values will differ, depending upon the type of imaging member selected.

The latent image comprising three levels of potential, hereinafter referred to as a tri-level image, may be formed on the imaging member by any of various suitable methods, such as those disclosed in US-A-4,078,929. For example, a tri-level charge pattern may be formed on the imaging member by the xerographic method of first uniformly charging the imaging member in the dark to a single polarity, followed by exposing the member to an original having areas both lighter and darker than the background area, such as a piece of gray paper having both white and black images thereon. In a preferred embodiment, a tri-level charge pattern may be formed by means of a raster output scanner, optically modulating laser light as it scans a uniformly charged photoconductive imaging member. In this embodiment, the areas of high potential are formed by turning the light source off, the areas of intermediate potential are formed by exposing the imaging member to the light source at partial power, and the areas of low potential are formed by exposing the imaging member to the light source at full power. Other electrophotographic and ionographic methods of generating latent images are also acceptable.

Generally, in the process of the present invention the highlighted areas of the image are developed with a developer of the present invention having a first color, usually other than black, while the remaining portions of the image are developed with a developer of a second color, usually black, although another color can also be selected. For the purpose of simplicity in describing the present invention, the first color toner will be referred to as the "color toner" or the "colored

toner" and the second color toner will be referred to as the "black toner", although either developer may be of any color. In general, the highlighted color portions are developed first to minimize the interaction between the two developers, thereby maintaining the high quality of the black image.

Development is generally by the magnetic brush development process disclosed in US-A-2,874,063. This method entails the carrying of a developer material containing toner and magnetic carrier particles by a magnet. The magnetic field of the magnet causes alignment of the magnetic carriers in a brushlike 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. Conductive magnetic brush development is generally employed for the process of the present invention in view of the relatively small development potentials of around 200 volts that are generally available for the process; conductive development ensures that sufficient toner is laid on the photoreceptor under these development potentials to result in acceptable image density. Conductive development is also preferred to ensure that fringe fields occurring around the edges of images of one color are not developed by the toner of the other color.

During the development process, the developer housings are biased to a voltage between the level of potential being developed and the intermediate level of charge on the imaging member. For example, if the latent image consists of a high level of potential of about -800 volts, an intermediate level of potential of about -400 volts, and a low level of about -100 volts, the developer housing containing the positively charged toner that develops the high areas of potential may be biased to about -500 volts and the developer housing containing the negatively charged toner that develops the low areas of potential may be biased to about -300 volts. These biases result in a development potential of about -200 volts for the high areas of potential, which will be developed with a positively charged toner, and a development potential of about + 200 volts for the low areas of potential, which will be developed with a negatively charged toner. Background deposits are suppressed by keeping the background intermediate voltage between the bias on the color developer housing and the bias on the black developer housing. Generally, it is preferred to bias the housing containing the positive toner to a vol-

tage of from about 100 to about 150 volts above the intermediate level of potential and to bias the housing containing the negative toner to a voltage of from about 100 to about 150 volts below the intermediate level of potential, although these values may be outside these ranges provided that the objectives of the present invention are achieved.

The developed image is then transferred to any suitable substrate, such as paper, transparency material, and the like. Prior to transfer, it is preferred to apply a charge by means of a corotron to the developed image in order to charge both toners to the same polarity, thus enhancing transfer. 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.

Black developers suitable for the process of the present invention comprise a toner and a carrier. A preferred carrier generally comprises a steel core, such as Hoeganaes Anchor Steel Grit, with an average diameter of from about 25 to about 215 microns, preferably from about 50 to about 150 microns, with a coating of chlorotrifluoroethylene-vinyl chloride copolymer, commercially available as OXY 461 from Occidental Petroleum Company, said coating containing from 0 to about 40 percent by weight of conductive particles homogeneously dispersed in the coating, at a coating weight of from about 0.4 to about 1.5 percent by weight. This coating is generally solution coated onto the carrier core from a suitable solvent, such as methyl ethyl ketone or toluene. Alternatively, the carrier coating may comprise a coating of polyvinyl fluoride, commercially available as Tedlar® from E.I. Du Pont de Nemours and Company, present in a coating weight of from about 0.01 to about 0.2, and preferably about 0.05, percent by weight of the carrier. The polyvinyl fluoride coating is generally coated onto the core by a powder coating process, wherein the carrier core is coated with the polyvinyl fluoride in powder form and subsequently heated to fuse the coating. In one preferred embodiment, the carrier comprises an unoxidized steel core which is blended with polyvinyl fluoride (Tedlar®), wherein the polyvinyl fluoride is present in an amount of about 0.05 percent by weight of the core. This mixture is then heat treated in a kiln at about 204°C to fuse the polyvinyl fluoride coating to the core. The resulting carrier exhibits a conductivity of about 7.6×10^{-10} (ohm-cm)⁻¹. Optionally, an additional coating of polyvinylidene fluoride, commercially available as Kynar® from Pennwalt Corporation, may be powder coated on top of the other coating of the carrier in the black developer at a coating weight of from about 0.01 to about 0.2 percent by weight. The carrier for the black developer

generally has a conductivity of from about 10^{-14} to about 10^{-7} , and preferably from about 10^{-12} to about 10^{-9} (ohm-cm)⁻¹.

Black toners suitable for development of the image generally comprise a resin, a pigment, and a charge control additive. Suitable resins include polyesters, styrene-butadiene polymers, styrene acrylate polymers, and styrene-methacrylate polymers, and particularly styrene-n-butylmethacrylate copolymers wherein the styrene portion is present in an amount of from about 50 to about 80 percent by weight, preferably about 58 percent by weight, and the n-butylmethacrylate portion is present in an amount of from about 20 to about 50 percent by weight, preferably about 42 percent by weight. Generally, the resin is present in an amount of from about 80 to about 98.8 percent by weight, and preferably in an amount of 92 percent by weight. Suitable pigments include those such as carbon black, including Regal® 330, commercially available from Cabot Corporation, as well as any pigment colored other than black. Generally, the pigment is present in an amount of from about 1 to about 15 percent by weight, and preferably in an amount of about 6 percent by weight.

Suitable charge control agents for the black toner of the present invention include distearyl dimethyl ammonium methyl sulfate and alkyl pyridinium halides such as cetyl pyridinium chloride and the like. The charge control agent is present in an amount of from about 0.1 to about 6 percent by weight, and preferably in an amount of about 2 percent by weight. In addition, the black toner may contain magnetite, such as Mapico Black, in an amount of from about 8 to about 20, and preferably about 15 or 16 percent by weight. A toner suitable for the present invention containing magnetite generally comprises from about 71.25 to about 87.8 percent by weight of the resin, from about 8 to about 20 percent by weight of the magnetite, from about 4 to about 7 percent by weight of carbon black, and from about 0.2 to about 1.75 percent by weight of the charge control additive.

In addition, external additives of colloidal silica, such as Aerosil® R972, Aerosil® R976, Aerosil® R812, and the like, available from Degussa, and metal salts or metal salts of fatty acids, such as zinc stearate, magnesium stearate, and the like, may optionally be blended on the surface of the black toner. Generally, the silica is present in an amount of from about 0.1 to about 2 percent by weight of the toner and the zinc stearate is present in an amount of from about 0.1 to about 2 percent by weight of the toner. These additives function in the manner described for the color toners with respect to charge control, admix control, conductivity control, and the like.

The black toners of the present invention may also optionally contain as an external additive a linear polymeric alcohol comprising a fully saturated hydrocarbon backbone with at least about 80 percent of the

polymeric chains terminated at one chain end with a hydroxyl group. The linear polymeric alcohol is of the general formula $\text{CH}_3(\text{CH}_2)_n\text{CH}_2\text{OH}$, wherein n is a number from about 30 to about 300, and preferably from about 30 to about 50. Linear polymeric alcohols of this type are generally available from Petrolite Chemical Company as Unilin™. The linear polymeric alcohol is generally present in an amount of from about 0.1 to about 1 percent by weight of the toner.

Black developer compositions for the present invention generally comprise from about 1 to about 5 percent by weight of the toner and from about 95 to about 99 percent by weight of the carrier. The ratio of toner to carrier may vary, however, provided that the objectives of the present invention are achieved. For example, an imaging apparatus employed for the process of the present invention may be replenished with a colored developer comprising about 65 percent by weight toner and about 35 percent by weight carrier. The triboelectric charge of the black toners generally is from about + 10 to about + 30, and preferably from about + 13 to about + 18 microcoulombs per gram, although the value may be outside of this range provided that the objectives of the present invention are achieved. Particle size of the black toners is generally from about 8 to about 13 microns in volume average diameter, and preferably about 11 microns in volume average diameter, although the value may be outside of this range provided that the objectives of the present invention are achieved.

Coating of the carrier particles for the black developer may be by any suitable process, such as powder coating, wherein a dry powder of the coating material is applied to the surface of the carrier particle and fused to the core by means of heat, solution coating, wherein the coating material is dissolved in a solvent and the resulting solution is applied to the carrier surface by tumbling, or fluid bed coating, in which the carrier particles are blown into the air by means of an air stream, and an atomized solution comprising the coating material and a solvent is sprayed onto the air-borne carrier particles repeatedly until the desired coating weight is achieved.

The black toners may be prepared by processes such as extrusion, which is a continuous process that entails dry blending the resin, pigment, 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. External additives such as linear polymeric alcohols, silica, or zinc stearate are then blended with the classified toner in a powder blender. Subsequent admixing of the toners with the carriers, generally in amounts of from about 0.5 to about 5 percent by weight of the toner and from about 95 to about 99.5 percent by weight of the carrier, yields the developers suitable for the two-

color imaging process of the present invention.

Specific embodiments of the invention will now be described in detail. These examples are intended to be illustrative, and the invention is not limited to the materials, conditions, or process parameters set forth in these embodiments. All parts and percentages are by weight unless otherwise indicated.

EXAMPLE I

A toner composition was prepared containing 90.5 percent by weight of Pliotone® resin (available from Goodyear), 7.0 percent by weight of PV Fast Blue B2G-A pigment (available from Hoechst-Celanese), 2.0 percent by weight of Bontron E-88 aluminum compound charge control agent (available from Orient Chemical, Japan), and 0.5 percent by weight of cetyl pyridinium chloride charge control agent (available from Hexcel Corporation). The toner components were first dry blended and then melt mixed in an extruder. The extruder strands were cooled, chopped into small pellets, ground into toner particles, and then classified to narrow the particle size distribution. The toner particles had a particle size of 13.0 microns (by volume median). Subsequently, the toner particles were dry blended with silica particles (Aerosil® R972, available from Degussa) in an amount of 0.3 percent by weight of the toner particles, and zinc stearate (available from Synthetic Products) in an amount of 0.3 percent by weight of the toner particles.

A carrier composition was prepared by coating Hoeganoes Steel Grit cores (available from Hoeganoes) with a coating comprising 80 percent by weight of polymethyl methacrylate (available from E.I. Du Pont de Nemours & Company) and 20 percent by weight of Vulcan carbon black (available from Cabot Corp), wherein the core was present in an amount of 99.2 percent by weight and the coating was present in an amount of 0.8 percent by weight. Coating was carried out by a solution coating process from methyl ethyl ketone.

EXAMPLE II

A developer composition was prepared by mixing together 3 parts by weight of the toner with 100 parts by weight of the carrier particles. The developer thus prepared containing Bontron E-88 aluminum compound charge control agent was incorporated into a printer test fixture comprising an organic imaging member and two developer housings, wherein a two-color image can be developed in a single pass by having the imaging member bearing a tri-level latent image pass both developer housings sequentially, and the conductivity of the developer was measured as the printer test fixture was operated with a tri-level electrostatic latent image on the imaging member

having voltages of -700 V, -400 V, and -100 V, with the image at -100 V being developed by the blue toner containing the Bontron E-88. The log (base 10) of the developer conductivity (mho) was -9.0. For comparison purposes, the same measurement was made on a developer of the same composition with the exception that the toner contained no cetyl pyridinium chloride, 3 percent by weight of the Bontron E-88, and 90 percent by weight of the Pliotone® resin. The developer containing no cetyl pyridinium chloride exhibited a lower value of the logarithm (base 10) of the developer conductivity of -11.0. Thus, the developer containing both cetyl pyridinium chloride and the aluminum compound charge control agent exhibited a higher conductivity, as indicated by the lower absolute value of the logarithm of the developer conductivity. Higher conductivity is generally desirable for developer compositions employed in conductive development processes.

EXAMPLE III

Four developers were prepared by preparing toners as described in Example I containing Bontron E-88 aluminum compound charge control agent. Each toner contained the amounts of pigment and external additives described for the toner in Example I. The toners contained, respectively, 2 percent by weight of Bontron E-88 aluminum compound charge control agent, 0.25 percent cetyl pyridinium chloride, and 90.75 percent by weight of Pliotone®; 2 percent by weight of Bontron E-88 aluminum compound charge control agent, 0.5 percent by weight of cetyl pyridinium chloride, and 90.5 percent by weight of Pliotone®; 3 percent by weight of Bontron E-88 aluminum compound charge control agent, 0.25 percent by weight of cetyl pyridinium chloride, and 89.75 percent by weight of Pliotone®; and 3 percent by weight of Bontron E-88 aluminum compound charge control agent, 0.5 percent by weight of cetyl pyridinium chloride, and 89.5 percent by weight of Pliotone®. For comparison purposes, a fifth toner was prepared containing 3 percent by weight of Bontron E-88 aluminum compound charge control agent and 90 percent by weight of Pliotone®. Each of the five toners was then admixed with a carrier as described in Example I to form five developer compositions.

The developers were incorporated into the printer test fixture described in Example II and the toner-to-carrier ratios of the five developers were varied to determine the maximum amount of toner concentration that could be contained in each developer before fringe field development occurred. Fringe field development occurred when the blue developer formed a blue halo surrounding the black images formed during the two-color development process. In the test fixture, a tri-level image was generated on the imaging member. The color image was developed first with

the blue developer containing the Bontron E-88 aluminum compound charge control additive, followed by development of the black image with a black developer. The black developer contained a toner comprising 2 percent by weight of cetyl pyridinium chloride, 6 percent by weight of Regal® 330 carbon black (available from Cabot Corporation), and 92 percent by weight of a styrene/n-butylmethacrylate polymer containing 58 percent by weight of styrene and 42 percent by weight of n-butylmethacrylate. The toner particles had a particle size of 11.4 microns (by volume median). The black carrier comprised a Hoeganoes steel core (as described for the carrier in Example I) coated with a polyvinyl fluoride (Tedlar®, available from E.I. Du Pont de Nemours & Company) coating in a coating weight such that the carrier comprised 0.05 percent by weight of the coating and 99.95 percent by weight of the core. The black toner and black carrier were mixed together in relative amounts of 3 parts by weight of toner to 100 parts by weight of carrier. The maximum toner concentration possible without fringe field development for the blue developer containing no cetyl pyridinium chloride was 4.5 percent by weight of toner. In contrast, for the blue developers containing both the aluminum compound charge control agent and cetyl pyridinium chloride, the maximum toner concentrations possible without fringe field development were, respectively: greater than 8.6 percent by weight (toner containing 2 percent by weight of Bontron E-88 and 0.25 percent by weight of cetyl pyridinium chloride); greater than 6.5 percent by weight (toner containing 2 percent by weight of Bontron E-88 and 0.5 percent by weight of cetyl pyridinium chloride); greater than 6.5 percent by weight (toner containing 3 percent by weight of Bontron E-88 and 0.25 percent by weight of cetyl pyridinium chloride); and greater than 6.7 percent by weight (toner containing 3 percent by weight of Bontron E-88 and 0.5 percent by weight of cetyl pyridinium chloride). These results indicate that the toner-to-carrier ratio of the developers containing both the aluminum compound charge control agent and cetyl pyridinium chloride can be varied over a wider range than the toner-to-carrier ratio of the developer containing only the aluminum compound charge control agent. This wider range over which toner-to-carrier ratio can be varied enables the developer to be adjusted to the varying temperature and relative humidity conditions under which development occurs without the occurrence of fringe field development.

EXAMPLE IV

The four developers in which the toners contained both the aluminum compound charge control agent and cetyl pyridinium chloride described in Example III were each roll milled for 30 minutes at a milling speed of 90 linear feet per minute, after which the

charging characteristics of the toners were measured. For comparison purposes, the charging characteristics of a developer in which the toner contained the aluminum compound charge control agent but no cetyl pyridinium chloride as described in Example III were also measured subsequent to milling. The A_t values of the four toners containing both the aluminum compound charge control additive and cetyl pyridinium chloride ranged from 75 to 83% $\mu\text{C/g}$; in contrast, the A_t value of the toner containing no cetyl pyridinium chloride was 70% $\mu\text{C/g}$, indicating that the toners containing both the aluminum compound charge control agent and cetyl pyridinium chloride were capable of becoming more highly charged than the toner containing no cetyl pyridinium chloride. A_t is a measure of triboelectric charging, and is calculated from the triboelectric charge in microcoulombs per gram and the toner concentration as follows:

$$A_t = \text{tribo } (\mu\text{C/g}) \times [\text{toner concentration } (\%) + 1]$$

EXAMPLE V

The admix performances of the developer in which the toner contained the aluminum compound charge control agent but no cetyl pyridinium chloride and the four developers in which the toners contained both the aluminum compound charge control agent and cetyl pyridinium chloride described in Example III were measured by introducing each developer into a roll mill at a toner concentration of 2.5 parts by weight of toner to 100 parts by weight of carrier, adding to the developer mixture fresh uncharged toner particles in an amount of 1 part by weight of toner, and roll milling the developer at 90 linear feet per minute until the fresh toner particles became fully charged. For the four developers in which the toners contained both the aluminum compound charge control agent and cetyl pyridinium chloride, admix was accomplished in 15 seconds. In contrast, for the developer in which the toner contained the aluminum compound charge control agent but no cetyl pyridinium chloride, admix was accomplished in 30 seconds, indicating that the presence of both the aluminum compound charge control agent and cetyl pyridinium chloride in the toner enabled more rapid admix.

EXAMPLE VI

A toner composition was prepared as described in Example I with the exception that the toner contained 3 percent by weight of Bontron E-84 zinc compound charge control agent (available from Orient Chemicals, Japan), 0.5 percent by weight of cetyl pyridinium chloride, and 89.5 percent by weight of Plio-tone®. This toner was admixed with the carrier prepared as described in Example I and the admix time for the resulting developer was measured by the process described in Example V. The admix time for

this developer was 15 seconds.

EXAMPLE VII

Three developers were prepared by preparing toners as described in Example I but containing Bontron E-84 zinc compound charge control agent instead of Bontron E-88 aluminum compound charge control agent. Each toner contained the amounts of pigment and external additives described for the toner in Example I. The toners contained, respectively, 3 percent by weight of Bontron E-84 zinc compound charge control agent, 0.5 percent cetyl pyridinium chloride, and 89.5 percent by weight of Pliotone®; 2 percent by weight of Bontron E-84 zinc compound charge control agent, 0.5 percent by weight of cetyl pyridinium chloride, and 90.5 percent by weight of Pliotone® and 2 percent by weight of Bontron E-88 aluminum compound charge control agent, 0.5 percent by weight of cetyl pyridinium chloride, and 90.5 percent by weight of Pliotone® (prepared by a process wherein the toner pellets obtained from the extruder were converted to powder particles with an Alpine Fluid Bed Grinder). The toner particles had a particle size of 13.0 microns (by volume median). Each of the three toners was then admixed with a carrier as described in Example I to form three developer compositions.

The developers were incorporated into the printer test fixture described in Example II and the toner-to-carrier ratios of the three developers were varied to determine the maximum amount of toner concentration that could be contained in each developer before fringe field development occurred, as described in Example III. The maximum toner concentration possible without fringe field development for all three developers was greater than 6.5 percent by weight of toner. In contrast, the developer described in Example III containing only Bontron E-88 aluminum compound charge control agent and no cetyl pyridinium chloride had a maximum toner concentration of 4.95 percent without fringe field development. These results indicate that the toner-to-carrier ratio of the developers containing both the zinc compound charge control agent and cetyl pyridinium chloride can be varied over a wider range than the toner-to-carrier ratio of the developer containing only the aluminum compound charge control agent.

EXAMPLE VIII

A developer was prepared by preparing a toner as described in Example I but containing Bontron E-84 zinc compound charge control agent instead of Bontron E-88 aluminum compound charge control agent and containing no cetyl pyridinium chloride. The toner contained 3 percent by weight of Bontron E-84 zinc compound charge control agent; 90 percent by weight of Pliotone®, and the amounts of pigment and exter-

nal additives set forth for the toner in Example I. The toner was then admixed with a carrier as described in Example I to form a developer composition.

The developer was incorporated into the printer test fixture described in Example II and the toner-to-carrier ratio of the developer was varied to determine the maximum amount of toner concentration that could be contained in the developer before fringe field development occurred, as described in Example III. The maximum toner concentration possible without fringe field development for this developer containing the zinc compound charge control agent was greater than 6.5 percent by weight of toner. In contrast, the developer described in Example III containing only Bontron E-88 aluminum compound charge control agent and no cetyl pyridinium chloride had a maximum toner concentration of 4.95 percent without fringe field development. These results indicate that the toner-to-carrier ratio of the developer containing the zinc compound charge control agent can be varied over a wider range than the toner-to-carrier ratio of the developer containing only the aluminum compound charge control agent.

EXAMPLE IX

Four developers in which the toners contained both the Bontron E-88 aluminum compound charge control agent and distearyl dimethyl ammonium bisulfate were prepared by the method described in Example I. Each toner contained the amounts of pigment and external additives described for the toner in Example I. The toners contained, respectively: 2 percent by weight of Bontron E-88 aluminum compound charge control agent, 0.25 percent distearyl dimethyl ammonium bisulfate (available from Hexcel Corporation), and 90.75 percent by weight of Pliotone®; 2 percent by weight of Bontron E-88 aluminum compound charge control agent, 0.75 percent by weight of distearyl dimethyl ammonium bisulfate, and 90.25 percent by weight of Pliotone®; 3 percent by weight of Bontron E-88 aluminum compound charge control agent, 0.25 percent by weight of distearyl dimethyl ammonium bisulfate, and 89.75 percent by weight of Pliotone®; and 3 percent by weight of Bontron E-88 aluminum compound charge control agent, 0.75 percent by weight of distearyl dimethyl ammonium bisulfate, and 89.25 percent by weight of Pliotone®. For comparison purposes, a fifth toner was prepared containing 3 percent by weight of Bontron E-88 aluminum compound charge control agent and 90 percent by weight of Pliotone®. Each of the five toners was then admixed with a carrier as described in Example I to form five developer compositions. The five developers were each roll milled for 30 minutes at a milling speed of 90 linear feet per minute, after which the charging characteristics of the toners were measured. The A_g values of the four toners containing both

the aluminum compound charge control additive and distearyl dimethyl ammonium bisulfate ranged from 82 to 90% $\mu\text{C/g}$; in contrast, the A_t value of the toner containing only the Bontron E-88 aluminum compound charge control agent was 70% $\mu\text{C/g}$, indicating that the toners containing both the aluminum compound charge control agent and distearyl dimethyl ammonium bisulfate were capable of becoming more highly charged than the toner containing no distearyl dimethyl ammonium bisulfate.

EXAMPLE X

The admix performances of the developer in which the toner contained the aluminum compound charge control agent but no distearyl dimethyl ammonium bisulfate and the four developers in which the toners contained both the aluminum compound charge control agent and distearyl dimethyl ammonium bisulfate described in Example IX were measured by introducing each developer into a roll mill, adding to the developer mixture fresh uncharged toner particles, and roll milling the developer at 90 linear feet per minute until the fresh toner particles became fully charged. For the four developers in which the toners contained both the aluminum compound charge control agent and distearyl dimethyl ammonium bisulfate, admix was accomplished in 15 seconds. In contrast, for the developer in which the toner contained the aluminum compound charge control agent but no distearyl dimethyl ammonium bisulfate, admix was accomplished in 30 seconds, indicating that the presence of both the aluminum compound charge control agent and distearyl dimethyl ammonium bisulfate in the toner enabled more rapid admix.

Claims

1. A toner composition comprising a resin, a colorant, a charge control additive comprising a mixture of (a) at least one first material selected from aluminum 3,5-di-tert-butyl salicylate compounds and zinc 3,5-di-tert-butyl salicylate compounds, and (b) at least one second material selected from alkyl pyridinium halides, distearyl dimethyl ammonium methyl sulfate, and distearyl dimethyl ammonium bisulfate, a colloidal silica external additive, and a metal salt of a fatty acid external additive
2. A toner composition according to claim 1 wherein the second material is cetyl pyridinium chloride.
3. A toner composition according to claim 1 or claim 2 wherein the resin is selected from polyesters, styrene-butadiene polymers, styrene-acrylate polymers, styrene-methacrylate polymers, and

mixtures thereof.

4. A toner composition according to any one of claims 1 to 3 wherein the pigment is selected from copper phthalocyanine pigments, substituted copper phthalocyanine pigments, halogenated copper phthalocyanine pigments, quinacridone pigments, azo pigments, rhodamine pigments, and mixtures thereof.
5. A toner composition according to any one of claims 1 to 4 wherein the total amount of charge control additive in the toner is from about 0.1 to about 10 percent by weight.
6. A toner composition according to any one of claims 1 to 5 wherein the second material is present in the toner in an amount of from about 0.1 to about 1 percent by weight.
7. A toner composition according to any one of claims 1 to 6 wherein the colloidal silica external additive is present in an amount of from about 0.1 to about 2 percent by weight of the toner.
8. A toner composition according to any one of claims 1 to 7 wherein the metal salt of a fatty acid external additive is present in an amount of from about 0.1 to about 2 percent by weight of the toner.
9. A developer composition comprising a toner according to any one of claims 1 to 8 and a carrier.
10. A developer composition according to claim 9 wherein the carrier comprises 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 polymethylmethacrylate 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.
11. An imaging process which comprises forming an electrostatic latent image on an imaging member, developing the latent image with the toner composition of any one of claims 1 to 8, transferring the developed image to a substrate, and optionally permanently affixing the transferred image to the substrate.
12. A process for forming two-color images which

comprises charging an imaging member, creating on the member a latent image comprising areas of high, medium, and low potential, developing the low areas of potential with a developer comprising a toner of a first color according to any one of claims 1 to 8 and a carrier, subsequently developing the high areas of potential with a developer comprising a toner of a second color and a carrier, transferring the developed two-color image to a substrate, and optionally permanently affixing the image to the substrate.

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European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 92 30 8029

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	US-A-4 837 101 (GRUBER ET AL.) * claims 1-18 *	1-12	G03G9/097
D,A	EP-A-0 414 502 (XEROX) * claims 1-12 * & US-A-4 904 762 (CHANG ET AL.)	1-12	
D,A	US-A-4 948 686 (KOCH ET AL.) * claims 1,14-24,27-30 *	1-12	
A	PATENT ABSTRACTS OF JAPAN vol. 15, no. 23 (P-1155)29 October 1990 & JP-A-22 64 970 (MITSUBISHI) 5 April 1989 * abstract *	1	
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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 25 NOVEMBER 1992	Examiner VOGT C.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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