

- [54] **ELECTROGRAPHIC CARRIER VEHICLE
AND DEVELOPER COMPOSITION**
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- [51] Int. Cl. **C03g 9/00**
- [58] Field of Search **252/62.1 P; 117/37 LE**

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[57] **ABSTRACT**

An electrographic carrier vehicle and developer composition containing said carrier vehicle are described. The carrier vehicle is composed of magnetically attractable core particles having thereon a metal ion-linked α -olefin-carboxylic acid copolymer coating containing finely-divided conductive particles dispersed therein.

10 Claims, No Drawings

ELECTROGRAPHIC CARRIER VEHICLE AND DEVELOPER COMPOSITION

This is a division of application Ser. No. 236,584 filed Mar. 21, 1972, now abandoned.

This invention relates to electrography and to a particulate carrier vehicle and a dry electrographic developer composition containing such a carrier vehicle useful in the development of latent electrostatic charge images.

Electrographic imaging and developing processes, e.g., electrophotographic imaging processes and techniques, have been extensively described in both the patent and other literature, for example, U.S. Pat. Nos. 2,221,776 issued Nov. 19, 1940; 2,277,013 issued Mar. 17, 1942; 2,297,691 issued Oct. 6, 1942; 2,357,809 issued Sept. 12, 1944; 2,551,582 issued May 8, 1951; 2,825,814 issued Mar. 4, 1958; 2,833,648 issued May 6, 1958; 3,220,324 issued Nov. 30, 1965; 3,220,831 issued Nov. 30, 1965; 3,220,833 issued Nov. 30, 1965 and many others. Generally these processes have in common the steps of forming a latent electrostatic charge image on an insulating electrographic element. The electrostatic latent image is then rendered visible by a development step in which the charged surface of the photoconductive element is brought into contact with suitable developer mix.

One method for applying the developer mix is by the well-known magnetic-brush process. Such a process generally utilizes apparatus of the type described, for example, in U.S. Pat. No. 3,003,462 issued Oct. 10, 1961 and customarily comprises a non-magnetic rotatably mounted cylinder having fixed magnetic means mounted inside. The cylinder is arranged to rotate so that part of the surface is immersed in or otherwise contacted with a supply of developer mix. The granular mass comprising the developer mix is magnetically attracted to the surface of the cylinder. As the developer mix comes within the influence of the field generated by the magnetic means within the cylinder, the particles thereof arrange themselves in bristle-like formations resembling a brush. The bristle formations that are formed by the developer mix tend to conform to the lines of magnetic flux, standing erect in the vicinity of the poles and laying substantially flat when said mix is outside the environment of the magnetic poles. Within one revolution the continually rotating cylinder picks up developer mix from a supply source and returns part or all of this material to the supply. This mode of operation assures that fresh mix is always available to the surface of the photoconductive element at its point of contact with the brush. In a typical rotational cycle, the roller performs the successive steps of developer mix pickup, brush formation, brush contact with the electrographic element, e.g., a photoconductive element, brush collapse and finally mix release.

In magnetic-brush development of electrostatic images the developer is commonly a triboelectric mixture of fine toner powder comprised, for example, of a dyed or pigmented thermoplastic resin with coarser carrier particles of a magnetic material such as iron particles, etc.

In magnetic brush development as well as in various other different types of electrographic development wherein a dry triboelectric mixture of a particulate carrier vehicle and a fine toner powder are utilized, it is advantageous to modify the surface properties of the particulate carrier vehicle so that a high net electrical

charge is imparted to the toner powder. Particulate carrier particles capable of imparting a relatively stable, high net electrical charge to the toner powder aid in improving retention of the toner to the carrier vehicle and thereby aid in reducing the amount of undesired "toner throw-off," i.e. the amount of toner powder thrown out of the developer mix as it is agitated in an electrographic development apparatus. Aside from the extraneous contamination problems inherent with airborne toner dust in the apparatus, "toner throw-off" also leads to imaging problems such as unwanted background and scumming of the electrostatic image-bearing element.

A variety of methods and materials for modifying the surface properties of particulate electrographic carrier vehicles have been proposed. See, for example, Miller, U.S. Pat. No. 3,547,822 issued Dec. 15, 1970, describing certain carboxylated resins useful for coating a particulate carrier vehicle; Miller, U.S. Ser. No. 119,061 filed Feb. 25, 1971, which describes magnetic carrier particles having two or more coatings of a resinous material applied thereon such that there is no substantial dissolution of one resinous layer into an adjacent resin layer; Miller, U.S. Pat. No. 3,632,512 issued Jan. 4, 1972, describing methods of treating and coating iron particles utilizing an acid wash followed by controlled drying and, if desired, a subsequent coating operation to product a particulate iron carrier vehicle having improved surface characteristics. Miller, U.S. Ser. No. 100,299 filed Dec. 21, 1970, describes a particulate carrier vehicle bearing an improved, highly conductive overcoat. Various other literature relating, in part, to varying the surface characteristics of a particulate carrier vehicle include U.S. Pat. Nos. 2,618,551 issued Nov. 18, 1952; 2,618,552 issued Nov. 18, 1952; 2,753,308 issued July 3, 1956; 2,874,063 issued Feb. 17, 1959; 2,880,696 issued Apr. 7, 1959; 3,202,093 issued Aug. 24, 1965; 3,526,533 issued Sept. 1, 1970; 3,533,835 issued Oct. 13, 1970; British Pat. No. 1,174,571 dated Dec. 17, 1969; and Canadian Pat. No. 835,317 issued Feb. 24, 1970.

In accordance with the present invention, it has been discovered that core particles having on the outer surface thereof a resinous coating of an ionomeric carboxylic acid — α -olefin copolymer with finely-divided electrically conductive particles dispersed therein provide an effective particulate carrier vehicle for an electrographic developer.

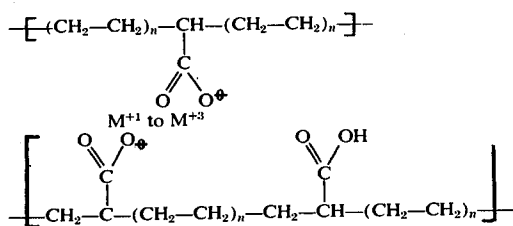
According to one embodiment of the invention, the aforesaid resinous ionomeric coating is provided as an outer coating for magnetically-attractable core particles. The resultant ionomeric-coated magnetically-attractable carrier particles, when admixed with a fine toner powder to form an electrographic developer composition, are especially useful in a magnetic-brush electrographic development process.

The incorporation of finely-divided electrically conductive particles, such as carbon black particles, in the ionomeric coated carrier of the invention provides a particulate carrier which, when admixed with a suitable toner powder, provides improved solid area image development without effecting a substantial change in the net electrical charge imparted to the toner powder. This result represents an unexpected and surprising discovery. That is, it is generally recognized in the art that the addition of even relatively small quantities of finely-divided electrically conductive particles, such as car-

bon black, to conventional resin-coated carrier particles ordinarily substantially reduces the static triboelectric value of the carrier coating; therefore, the net electrical charge imparted to toner powder admixed with such a carrier vehicle is also substantially reduced. (See U.S. Pat. No 3,533,835 at Col. 10 and Example II-VII thereof).

The ionomeric materials useful as polymeric coatings for the carrier particles of the invention comprise ionic copolymers of (a) an α -olefin having the general formula $RCH=CH_2$ where R is a radical selected from the class of hydrogen and alkyl radicals having from 1 to about 8 carbon atoms and (b) an α,β -ethylenically unsaturated carboxylic acid having from 3 to about 8 carbon atoms, said copolymers having from 10 to about 90% of the carboxylic acid groups ionized with metal ions. The ionomers are typically formed by "neutralization" of a base α -olefin-carboxylic acid copolymer with an ionizable metal compound. The unsaturated carboxylic acid content of the copolymer is typically from about 0.2 to 25 mole percent based on the α -olefin-acid base copolymer, and the α -olefin content of the copolymer is at least 50 mole percent based on the α -olefin-acid base copolymer. Especially useful in the invention are ionomeric, carboxylic acid α -olefin copolymers having a free acid content less than about 2 milliequivalents of 1N NaOH per gram of the ionomeric copolymer based on the dry weight of the ionomer. Typically, the carboxylic acid groups contained in the ionomeric materials useful in the invention are randomly distributed throughout the polymeric structure.

Ionomeric materials which have been found to provide especially good results according to the present invention are ionomeric carboxylic acid-ethylene copolymers having recurring structural units which are conventionally represented in the literature as follows:



wherein M^{+1} to M^{+3} is a metallic ion and n is an integer within the range of 1 to about 20 or more.

As can be seen by the above structural formula, the metal ions contained in the ionomeric materials are believed to provide ionic crosslinking. Metals especially useful as the metal ions contained within the ionomeric materials are alkali metal ions including Na^+ , K^+ , Li^+ , and Cs^+ . However, a variety of other metallic ions may also be used including complexed and uncomplexed metal ions.

When using the uncomplexed metal ions the valence of the ion corresponds to the valence of the metal. These metal ions are obtained from the commonly known and used metal salts. The complexed metal ions are those in which the metal is bonded to more than one type of salt group, at least one of which is ionized and at least one of which is not. Since the formation of the ionic copolymers requires only one ionized valence state, it will be apparent that such complexed metal ions are equally well suited in the present invention.

The term "metal ion having one or more ionized valence states" means a metal ion having the general formula Me^{+n}X_m , where n is the ionic charge and is at least one, X is a nonionized group and $n+m$ equal the valence of the metal. The utility of complexed metal ions employed in the formation of ionic copolymers corresponds in their ionized valences to those of the uncomplexed metal ions. The monovalent metals are, of course, excluded but higher valent metals may be included depending on how many metal valences are complexed and how many can be ionized. The preferred complexed metal ions are those in which all but one metal valences are complexed and one is readily ionized. Such compounds are in particular the mixed salts of very weak acids, such as oleic and stearic acid, with ionizable acids, such as formic and acetic acid.

The uncomplexed metal ions which are suitable in forming the ionic copolymers used in the present invention comprise mono- di- and trivalent ions of metals in Groups I, II, III, IV-A and VIII of the Periodic Table of Elements (see page 392, *Handbook of Chemistry and Physics*, Chemical Rubber Publishing Co., 37th ed.). Suitable monovalent metal ions are Na^+ , K^+ , Li^+ , Cs^+ , Ag^+ , Hg^+ and Cu^+ . Suitable divalent metal ions are Be^{+2} , Mg^{+2} , Ca^{+2} , Sr^{+2} , Ba^{+2} , Cu^{+2} , Hg^{+2} , Sn^{+2} , Pb^{+2} , Fe^{+2} , Cd^{+2} , Co^{+2} , Ni^{+2} and Zn^{+2} . Suitable trivalent metal ions are Al^{+3} , Sc^{+3} , Fe^{+3} and Y^{+3} .

The quantity of ions employed or the degree of neutralization will differ with the degree of solid property change and the degree of melt property change desired in the resultant ionomeric material. In general, it has been reported that the concentration of the metal ion should be at least such that the metal ion neutralizes at least 10 percent of the carboxylic acid groups in order to obtain a significant change in properties. The degree of neutralization for optimum properties will vary with the acid concentration and the molecular weight of the base copolymer. However, it is generally reported desirable to neutralize at least 50 percent of the acid groups. The degree of neutralization may be measured by several techniques. Thus, infrared analysis may be employed and the degree of neutralization calculated from the changes resulting in the absorption bands. Another method comprises the titration of a solution of the ionic copolymer with a strong base. In general, it has been reported that the added metal ion reacts stoichiometrically with the carboxylic acid in the base polymer up to 90 percent neutralizations. Small excess quantities of the crosslinking agent are necessary to carry the neutralization to completion. However, large excess quantities of the crosslinking agent do not add to the properties of the ionic copolymer, since once all carboxylic acid groups have been ionically crosslinked, no further crosslinks are formed.

As stated above, especially useful ionomeric materials in the present invention are those in which the resultant ionomer has a free acid content less than about 2 milliequivalents of 1N NaOH per gram of the ionomeric copolymer based on the dry weight of the ionomer. Such ionomeric coated carrier particles have been found to impart a high net electrical charge to the toner material and produce extremely small amounts of "toner throw-off" in a magnetic brush development apparatus.

The α -olefin polymers employed in the formation of the base copolymers are α -olefins which have the general formula $RCH=CH_2$ where R is either a hydrogen

or an alkyl group having preferably from 1 to 8 carbon atoms. Thus, suitable olefins include ethylene, propylene, butene-1, pentene-1, hexene-1, heptene-1, 3-methylbutene-1, 4-methylpentene-1, etc. Although olefins having higher carbon numbers can be employed, they are not materials which are readily obtained or available. The concentration of the α -olefin is at least 50 mol percent in the base copolymer, and is preferably greater than 80 mol percent.

The second component employed in the formation of the base copolymer comprises an α,β -ethylenically unsaturated carboxylic acid having preferably from 3 to 8 carbon atoms. Examples of such monomers are acrylic acid, methacrylic acid, ethacrylic acid, itaconic acid, maleic acid, fumaric acid, monoesters of said dicarboxylic acids, such as methyl hydrogen maleate, methyl hydrogen fumarate, ethyl hydrogen fumarate and maleic anhydride. Although maleic anhydride is not a carboxylic acid in that it has no hydrogen attached to the carboxyl groups, it can be considered an acid for present purposes because of its chemical reactivity being that of an acid. Similarly, other α,β -monoethylenically unsaturated anhydrides of carboxylic acids can be employed. As indicated, the concentration of acidic monomer in the base copolymer is from 0.2 mol percent to 25 mol percent, and, preferably, from 1 to 10 mol percent.

Greater detail concerning the ionomeric (i.e., ion-linked) materials useful in the present invention may be found in Rees, U.S. Pat. No. 3,264,272 issued Aug. 2, 1966, incorporated herein by reference thereto.

In accordance with the present invention, ionomeric coating material is applied to a core particle in the form of an aqueous-alcoholic dispersion containing finely-divided particles of the ionomer dispersed therein. Typically, a surfactant is also present to aid in the formation and stabilization of the aqueous ionomeric dispersion. Typically, the aqueous-alcoholic ionomer dispersions have a solids content ranging from about 10 to about 60 percent by weight. The particle size of the ionomeric material dispersed therein is reported to vary from about 0.02 to 0.6 microns, generally from 0.1 to 0.6 microns. The pH of the ionomeric dispersion is typically basic in character varying from about 7.0 to about 12. The melt viscosity of a typical dry ionomeric coating on a carrier core particle is on the order of about 5×10^3 poise as measured at 150°C. at a shear rate of 300 sec. The dispersions are typically applied to the core particles to be coated at a temperature within the range of from roughly 25° to about 85°C. When so applied, a thin highly adherent film of the ionomeric material is formed which may cover all or only certain portions of the outer surface of the core particles. Once applied, the coating may be heated up to about 140°C. to develop optimum film strength and to dry the coating. No special binding agents are necessary to adhere the ionomeric resin to the magnetic core particles thus providing one of the advantages of the invention.

The ionomer dispersion may be applied to the core particle by any known coating technique, e.g., by a fluidized bed coating process. It may be applied by passing the particulate material to be coated through a bath containing the coating composition, in a continuous manner or in a batch manner. The coating may also be sprayed on the film, or applied manually by brushing or the like.

The amount of the ionomeric materials coated on the carrier core particles may vary from about 0.001 to about 3 percent by weight based on the total weight of the carrier particles. For example, on sponge iron core particles it appears that dry ionomeric coatings in the range of about 0.05 to about 0.60 percent by weight based on the total weight of the coated carrier is desirable. Especially good results have been obtained utilizing on sponge iron particles ionomeric coatings comprising 0.15 to 0.30 percent by weight of the coated carrier particle. Although more or less of the ionomeric coating may be utilized if desired, it appears that, for example, on sponge iron particle levels below about 0.05 percent start to exhibit an increase in "toner throw-off" while levels above about 0.60 percent do not appear to provide as good development of solid area images as is otherwise obtainable.

As indicated above, in accordance with the invention, finely-divided electrically conductive particles such as carbon black are incorporated in the ionomeric coating. A variety of different methods for incorporating such additives may be used. One useful method simply involves admixing the electrically conductive particulate additive into the ionomeric dispersion prior to its application on the particulate carrier core particles. Typically, these electrically conductive particles have a particle size within the range of from about 1 to about 20 microns. The electrically conductive particles have a specific resistance less than about 10 ohm-cm., typically as in the case of carbon black, less than 1 ohm-cm. (Specific resistance as used herein is measured at room temperature.) Useful amounts of the electrically conductive particles incorporated in the ionomeric coating of the invention are generally within the range of from about 1 to about 50 parts by weight of conductive particles per 100 parts by weight of ionomer coating (based on the dry weight of the ionomeric coating).

Advantageously, the core materials which can suitably be coated to form carrier particles in accordance with this invention are magnetic materials. The phrase "magnetic materials" as used herein encompasses a variety of magnetically attractable materials. Particularly useful materials would include ferromagnetic materials such as the metals of the first transition series, i.e., nickel, iron, cobalt, and alloys and mixtures thereof. Other useful materials which exhibit a net magnetic moment are the ferrimagnetic materials. Examples of such ferrimagnetic materials would include the ferrites, which are materials having the general formula $\text{MeO} \cdot \text{Fe}_2\text{O}_3$, where Me is a metal ion, as well as mixed ferrites, which contain more than one species of metal ion in addition to iron, and the substituted ferrites, in which another metal replaces some of the iron. Also included in the phrase magnetic material are particles such as those described in Miller, Canadian Pat. No. 835,317 issued Feb. 24, 1970, and which are comprised of, for example, iron dispersed in a resin binder. Such magnetic materials are used as a core in accordance with this invention over which is coated the above-described ionomeric resin. The core can consist of a solid particle of magnetic material or can be a nonmagnetic particle overcoated with ferromagnetic materials as described in Belgian Pat. No. 726,806, dated Mar. 14, 1969. The core can comprise rough-surfaced magnetically responsive particles; smooth-surfaced magnetically responsive particle; or a mixture of rough-surfaced and smooth-surfaced magnetically responsive particles.

Particles having these varying surface properties and mixtures thereof are more fully described in Trachtenberg et al., copending patent application U.S. Ser. No. 236,724 filed Mar. 21, 1972 and entitled "Electrographic Carrier Vehicle and Developer Composition — Case A."

A core can vary in size and shape with core particles having an average diameter of from about 1,200 to about 30 microns. Particularly good development is obtained with core materials of from about 300 to about 60 microns average diameter. The size of the core particles used will, of course, depend upon several factors such as the type of images ultimately developed, desired thickness of the ionomeric resin coating, etc. The phrase "average diameter" as used herein is not meant to imply that only perfectly uniformly dimensioned particles can be used. This phrase is used to refer to the average thickness of particles when measured along several axes. Average diameter also refers to the approximate size of the openings in a standard sieve series which would just retain or just pass a given particle. In addition, it may be noted that the core materials useful in the present invention may be subjected to various treatments to modify their surface properties prior to being coated with the above-described terpolymer. For example, it may be desirable to wash a magnetic core in an acid-wash, rinse and subject the washed particles to controlled drying conditions so as to induce or exclude oxidation of the surface of the carrier particles. Such treatments are especially useful when the magnetic core comprises iron particles. Such treatment processes are described more fully in Belgian Pat. No. 746,109 dated Apr. 30, 1970.

Electrostatic developer compositions of the present invention can be prepared by mixing from about 90 to about 99 percent by weight of the above-described carrier vehicle with from about 10 to about 1 percent by weight of a suitable electroscopic toner material.

The toner material (or marking particles) useful in dry electrographic developer compositions are generally comprised of a resin binder and a colorant. Suitable toners can be selected from a wide variety of materials to give desired physical properties to the developed image and the proper triboelectric relationship to match the carrier particles used. Generally, any of the toner powders known in the art are suitable for mixing in the developer composition of this invention. In certain instances, the toner may be comprised solely of colorant material without any resinous binder. In other cases, where a visible image is not desired or needed, the toner may be composed solely of a colorless material, such as a resinous material, having the desired physical and triboelectric properties.

When the toner powder selected is utilized with magnetic carrier particles in a magnetic-brush development arrangement, the toner clings to the carrier by triboelectric attraction. The carrier particles acquire a charge of one polarity and the toner acquires a charge of the opposite polarity. Thus, if the carrier is mixed with a resin toner which is higher in the triboelectric series, the toner normally acquires a positive charge and the carrier a negative charge.

Useful toner particles can be prepared by various methods. Two convenient techniques for preparing these toners are spray-drying or melt-blending followed by grinding. Spray-drying involves dissolving the resin, colorant and any additives in a volatile organic solvent

such as dichloromethane. This solution is then sprayed through an atomizing nozzle using a substantially non-reactive gas such as nitrogen as the atomizing agent. During atomization, the volatile solvent evaporates from the airborne droplets, producing toner particles of the uniformly colored resin. The ultimate particle size is determined by varying the size of the atomizing nozzle and the pressure of the gaseous atomizing agent. Further details relating to spray-drying may be found in Carlson, U.S. Pat. No. 2,357,809 issued Sept. 12, 1944. Conventionally, particles of a diameter between about $\frac{1}{2}\mu$ and about 30μ are used, with particles between about 2μ and 15μ being preferred, although larger or smaller particles can be used where desired for particular development or image considerations.

Suitable toners can also be prepared by melt-blending. This technique involves melting a powdered form of polymer or resin and mixing it with suitable colorants and additives. The resin can readily be melted or heated on compounding rolls which are also useful to mix or otherwise blend the resin and addenda so as to promote the complete intermixing of these various ingredients. After thorough blending, the mixture is cooled and solidified. The resultant solid mass is then broken into small pieces and finely ground to form a free-flowing powder of toner particles. Such a melt-blending technique is described in Walkup, U.S. Pat. No. 2,618,551 issued Nov. 18, 1951. Of course, various other techniques for making toner particles may also be used. For example, certain spray-freeze drying techniques may be modified to provide useful methods for preparing toner particles. An example of such a modified spray freeze drying technique is described in Product Licensing Index, Volume 84, Apr. 1971. The resultant toner particles usually range in size from about $\frac{1}{2}$ to about 38μ .

The resin material used in preparing the toner can be selected from a wide variety of materials, including natural resins, modified natural resins and synthetic resins. Exemplary of useful natural resins are balsam resins, colophony, and shellac. Exemplary of suitable modified natural resins are colophony-modified phenol resins and other resins listed below with a large proportion of colophony. Suitable synthetic resins are all synthetic resins known to be useful for toner purposes, for example, polymers, such as certain polycarbonate resins described in U.S. patent application Ser. No. 34,557 filed May 4, 1970, and in Product Licensing Index, Volume 84, April 1971, vinyl polymers and copolymers including polyvinyl chloride, polyvinylidene chloride, polyvinyl acetate, polyvinyl acetals, polyvinyl ether, polyacrylic and polymethacrylic esters, polystyrene, including substituted polystyrenes; polycondensates, e.g., polyesters, such as phthalate, terephthalic and isophthalic polyesters, malcinate resins and colophony-mixed esters of higher alcohols; phenolformaldehyde resins, including modified phenol-formaldehyde condensates; aldehyde resins; ketone resins; polyamides; polyurethanes, etc. Moreover, chlorinated rubber and polyolefins, such as various polyethylenes, polypropylenes, polyisobutylenes, are also suitable. Typical toner materials having incorporated therein styrene containing materials are disclosed in the following U.S. Pat. Nos.: 2,917,460, Solar, issued Dec. 15, 1959; Re.25,136, Carlson, issued Mar. 13, 1962; 2,788,288, Rheinfrank et al., issued Apr. 9, 1957; 2,638,416, Walkup et al., issued Apr. 12, 1953; 2,618,552, Wise,

issued Nov. 18, 1952; and 2,659,670, Copley, issued Nov. 17, 1953. Other useful styrene containing toner resins are copolymers prepared from a monomeric blend of (a) 40–60 percent by weight styrene or styrene homolog; (b) 20–50 percent by weight of lower alkyl acrylate and methacrylate, e.g., alkyl methacrylates and alkyl acrylates having up to 3 carbon atoms in the alkyl groups; and (c) 5–30 percent by weight of higher alkyl acrylates and methacrylates, e.g., alkyl methacrylates and alkyl acrylates having 6–20 or more carbon atoms in the alkyl group.

Colorants useful in the practice of this invention can be selected from a variety of materials such as dyestuffs or pigments. Such materials serve to color the toner and thus render it more visible. Suitable toner materials having appropriate caking and charging properties can, of course, be prepared without the use of a colorant material where it is desired to have a developed image of low optical opacity. In those instances where it is desired to have high optical opacity, the colorants used can, in principle, be selected from virtually all of the compounds mentioned in the *Colour Index*, Vols. I and II, Second Edition. Included among the vast number of useful colorants would be such materials as Hansa Yellow G (C.I. 11680), Nigrosine Spirit soluble (C.I. 50415), Chromogen Black ETOO (C.I. 14645), Rhodamine B (C.I. 45170), Solvent Black 3 (C.I. 26150), Fuchsin N (C.I. 42510), C.I. Basic Blue 9 (C.I. 52015), etc. Another useful class of colorants is comprised of nigrosine salts such as nigrosine salts of mono- and di-functional organic acids having from about 2 to about 20 carbon atoms such as chloroacetic acid, stearic acid, sebacic acid, lauric acid, azelaic acid, adipic acid, abietic acid and the like. Nigrosine salts of this type are disclosed in Belgian Pat. No. 734,570 dated Aug. 14, 1969. Carbon black also provides a useful colorant as disclosed in Walkup, U.S. Pat. No. 2,618,551 issued Nov. 18, 1952. The amount of colorant added may vary over a wide range, for example, from about 3 to about 20 percent of the weight of the resin binder. Particularly good results are obtained when the amount is from about 5 to about 10 percent. In certain instances, it may be desirable or preferred to omit the colorant, in which case the lower limit of concentration would be zero.

In addition, if desired, organic melt viscosity modifying agents for the resin binder may be incorporated in the toner particles. If such viscosity modifying agents are utilized, the ratio of melt viscosity modifying agent to resin binder generally can vary from about 1:3 to about 1.5:1. Further information concerning these viscosity modifying agents may be found in Merrill et al., U.S. application Ser. No. 23,031, filed Mar. 26, 1970.

The following examples are provided to further illustrate the present invention and certain advantages thereof:

EXAMPLE 1

This example illustrates certain of the unique electrical properties of the ionomeric coated carrier particles of the present invention. The example illustrates that even when relatively large amounts of finely-divided electrically conductive particulate matter such as carbon black are incorporated in the ionomeric coatings of the carrier particle, these coated carrier particles nevertheless impart relatively high net electrical charge to toner particles admixed with the ionomeric coated

carrier particles. In this example, a control toner composed of pigmented thermoplastic resin particles is used. The carrier particles are composed of sponge iron particles having an average diameter within the range of from 80 to 120 mesh. These sponge iron carrier particles are obtained from the Hoeganaes Corporation under the tradename of Hoeganaes EH iron particles. These sponge iron particles utilized in the example have an oxidized surface which may be obtained, for example, by treating these particles in an acid wash and drying in an oxygen-containing atmosphere as described in Belgian Pat. No. 746,109 dated Apr. 30, 1970. The oxidized sponge iron particles are then coated with an aqueous dispersion of an ionomeric, acid-modified ethylene copolymer. The dispersion of ionomeric material is purchased from the E. I. DuPont Company under the trademark Elvax D-1070. After coating the oxidized sponge iron particles with the aqueous dispersion of ionic material, the coated particles are dried to form the resultant carrier particles having coated on the outer surface thereof a tough, thin discontinuous coating of ionomeric material. When dry, the total amount of ionomeric material contained on the surface of the carrier particles is approximately 0.15 percent by weight based on the total weight of the coated carrier particles. A total of five different particulate carrier vehicles are made as described hereinabove, the only difference among the five carrier vehicles being the quantity of electrically conductive particles incorporated in the ionomeric coating. Each of the 5 carriers are then mixed with an identical amount of the control toner to form 5 separate developer mixes, each mix containing 5 percent by weight of toner. In each case the electrically conductive particles are incorporated in the resultant ionomeric coated carrier particles by admixing a suitable amount of finely-divided carbon particles in the aqueous dispersion of ionomeric material prior to the coating thereof on the oxidized iron core particle. The amount of finely-divided electrically conductive carbon particles incorporated in each of the ionomeric coated carrier vehicles utilized in this example are set forth immediately hereinbelow. The net toner charge, Q, imparted by each of the five carrier vehicles to the control toner is measured (using the technique described hereinafter).

TABLE I

Carrier Vehicle	Carbon Particles (parts by weight carbon particles per hundred parts by weight of dry ionomeric coating)	Net Toner Charge (microcoulombs/gram)
1	0	18.6
2	10	17.3
3	20	19.2
4	30	18.4
5	40	17.5

Observation of the above data collected in Table 1 hereinabove indicates that there is no significant decrease in the triboelectric charge imparted to a toner powder even when relatively large amounts of conductive carbon particles are incorporated in the ionomeric coated carrier particles of the invention. This unique property of the ionomeric coating carrier particles of the invention is surprising and unexpected in view of the teachings of the art which suggests that by incorpo-

rating conductive particles in a polymer coated carrier vehicle, the electrical charge imparted to the toner powder is substantially reduced.

In this example the net charge Q imparted to the toner powder is measured using a Farraday Cage in the following manner: A weighed portion of each of the developers is placed in an iron tube that is covered at one end with a 200 mesh screen that retains all carrier particles within the tube. An air stream is then directed through the tube, blowing toner particles off the carrier, through the 200 mesh screen at the exit and into a Farraday Cage condenser that is at an initial electrical potential of 0 volt as measured by an electrometer. As the triboelectrically charged toner particles settle on the walls of the cage, their electrical potential is measured by the electrometer. The potential obtained is converted to electrical charge in microcoulombs and this figure is divided by the weight in grams of the toner powder particles that have settled in the Farraday Cage, thus providing the net toner charge in microcoulombs per gram. The net toner charge is therefore the algebraic sum of the electrical charges on the toner particles which have settled on the walls of the case.

EXAMPLE 2

Each of the above-described carrier vehicles, i.e. Numbers 1-5 are then admixed with 5 percent by weight of a dry pigmented thermoplastic resinous toner powder and used in a magnetic-brush process to develop an electrostatic charge pattern carried on an electrophotographic film. In each case good electrophotographic images are obtained. It is observed that better development of solid area images is obtained by utilizing carrier vehicles Numbers 2-5 as described in Example 1 above which contain a quantity of electrically conductive particles incorporated in the ionomeric coated carrier vehicle.

The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

I claim:

1. In an electrographic developing composition for use in developing electrostatic charge patterns and comprising a physical mixture of magnetically attractable carrier particles and electroscopic toner particles, the improvement wherein said carrier particles comprise cores of magnetically-attractable material having thereon a resinous coating comprising

- a. a polymer comprising a metal ion-linked carboxylic acid α -olefin copolymer, said α -olefin having the formula $RCH=CH_2$ where R is a radical selected from the group consisting of hydrogen and alkyl radicals having from 1-8 carbon atoms, said carboxylic acid is selected from the group consisting of α,β -ethylenically unsaturated carboxylic acids having from 3 to about 8 carbon atoms said

copolymers having from 10 to about 90 percent of the carboxylic acid groups ionized with metal ions and

- b. finely-divided electrically conductive particles having a specific resistance less than 10 ohm-cm incorporated in said coating.

2. The invention of claim 1 wherein said α -olefin is ethylene and wherein said metal ions are alkali metal ions.

3. The invention of claim 1 wherein said copolymer has a free acid content of less than about 2 milliequivalents of 1N NaOH per gram of the ion-linked copolymer based on the dry weight of said copolymer.

4. The invention as described in claim 1 wherein the magnetically-attractable core contains a material selected from the group consisting of iron, nickel, cobalt and alloys and mixtures thereof.

5. The invention as described in claim 1 wherein the average size of the carrier core particle is from about 30 to about 1,200 microns.

6. An electrographic developer composition comprising a mixture of from about 1 to about 10 weight percent of electroscopic toner particles and from about 90 to about 99 weight percent of carrier particles wherein said carrier particles comprise cores of ferromagnetic material having thereon a coating comprising

- a. a polymer comprising a metal ion-linked carboxylic acid α -olefin copolymer, said α -olefin having the formula $RCH=CH_2$ where R is a radical selected from the group consisting of hydrogen and alkyl radicals having from 1 to about 8 carbon atoms, said carboxylic acid is selected from the group consisting of α,β -ethylenically unsaturated carboxylic acids having from 3 to about 8 carbon atoms, said copolymers having from 10 to about 90 percent of the carboxylic acid groups ionized with metal ions and

- b. finely-divided conductive particles having a specific resistance less than 10 ohm-cm incorporated in said coating.

7. The invention of claim 6 wherein the ferromagnetic material is selected from the group consisting of iron and iron alloys and wherein the average size of the carrier core particles is within the range of from about 60 to about 300 microns.

8. The invention of claim 6 wherein said polymer comprises from about 0.001 to about 3 percent by weight of the total weight of the coated carrier particle.

9. The invention of claim 6 wherein said polymer coating has incorporated therein from about 1 to about 50 parts by weight of electrically conductive particles per 100 parts by weight of the dry polymer coating, said conductive particles having a particle size within the range of from about 1 to about 20 microns and having a specific resistance less than about 10 ohm-cm.

10. The invention of claim 6 wherein said electrically conductive particles are carbon particles.

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