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3,809,554

DRY ELECTROSTATIC TONER COMPOSITION AND PROCESS OF DEVELOPING

Stewart H. Merrill and James R. Olson, Rochester, N.Y.,
assignors to Eastman Kodak Company, Rochester, N.Y.
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12 Claims

ABSTRACT OF THE DISCLOSURE

Uniformly charging electroscopic toner compositions for use in developing electrostatic charge patterns are described. Dry developer compositions containing a carrier and said uniformly charging toner are also described. The toner compositions contain aromatic resins characterized by a recurring unit containing alternating methylene groups and certain aromatic groups.

The present invention relates to the dry development of electrostatic latent images. Such images are formed, for example, on electrophotographic elements.

Electrophotographic elements or materials conventionally involve an electrically conducting support on which is coated a photoconductive insulating material. After overall charging such as by a corona source and an image-wise light exposure that discharges the photoconductor in the exposed areas, an electrostatic charge pattern remains. This electrostatic charge pattern as well as electrostatic charge patterns produced by other techniques, can be rendered visible by treatment with an electrostatic developing composition or developer. Conventional dry developers include a carrier that can be either a magnetic material such as iron filings, powdered iron or iron oxide, or a triboelectrically chargeable, non-magnetic substance like glass or plastic beads or crystals of inorganic salts such as sodium or potassium chloride. As well as the carrier, electrostatic developers include a toner that is usually a resinous material suitably darkened for image viewing purposes with a colorant like dyestuffs or pigments such as carbon black.

To develop an electrostatic charge pattern, the dry developer is applied to an imagewise electrostatically charged surface by techniques such as the magnetic brush means described in U.S. Pat. No. 3,003,462. The developer composition, including both toner and magnetic carrier particles, is maintained, during the development cycle, in a loose, brush-like orientation by a magnetic field surrounding, for example, a rotatable non-magnetic cylinder having a magnetic means fixedly mounted inside. The magnetic carrier particles are attracted to the cylinder by the described magnetic field, and the toner particles are held to the carrier particles by virtue of their opposite electrostatic polarity. Before and during development, the toner acquires an electrostatic charge of a sign opposite to that of the carrier material due to triboelectric charging derived from their mutual frictional interaction.

When this brush-like mass or magnetic brush of carrier and toner particles is drawn across the photoconductive surface bearing the electrostatic pattern, the toner particles are electrostatically attracted to an oppositely charged latent image and form a visible toner image corresponding to the latent image. If both charges are of a like sign, then the toner particles adhere to the photoconductor's discharged areas. In such fashion, it is possible to form either positive or negative reproductions.

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In the past, phenol-formaldehyde resins have been conventionally used as a resinous binder for electrostatic toners. However, when developing a latent electrostatic image using a toner composition containing a phenol-formaldehyde resin binder, it has been found that such toners tend to contain a number of particles having either a polarity opposite to that desired or a diminished net charge, although of the correct polarity. Such an occurrence is caused by the failure of the resultant toner material to charge uniformly, and it promotes the deposition of toner particles in background areas, impedes cleaning of reuseable photoconductor elements and also contributes to an undesirably weak attraction between toner and carrier, thereby promoting the formation of an image having either irregular density or other defects such as streaks, etc. Additionally, when development is by well-known magnetic brush techniques, non-uniformly charged toner particles tend to be thrown off a rotating magnetic brush and are thus not available for image development.

Moreover, it is often conventional practice to place a bias voltage of a polarity opposite to that of the toner particles across the magnetic brush. Such action provides additional attraction between toner particles and the magnetic brush apparatus and thereby tends to restrict background toning in exposed areas of the photoconductor or in the background area of any other insulating surface bearing a latent electrostatic image still possessing a residual charge. The bias voltage is not so great, however, as to interfere with the toning of desired image areas having a sufficient charge to attract and draw away toner particles from the carrier.

Where certain of the toner particles have an opposite polarity, as in non-uniform polarity toners, such particles are repelled from the magnetic brush by this bias voltage. In like fashion the intended image areas of the charged insulating surface, having a polarity similar to the "opposite polarity" toner particles, also exert a repelling force with the resulting deposition of "opposite polarity" toner particles in non-image or background areas.

Accordingly, it is an object of this invention to provide, for electrophotographic development purposes, new uniform-polarity toner materials.

It is another object of this invention to provide for electrophotographic development purposes, a novel toner containing a uniform-polarity resinous binder which has an increased resistance to background development.

An additional object of the present invention is to provide, for electrophotographic development purposes, a new uniform-polarity toner composition that promotes developed images of an increased and uniform density.

Still an additional object of this invention is to provide, for electrophotographic development purposes, a novel uniform-polarity toner composition that is resistant to magnetic brush throwoff.

A further object is to prepare improved electrostatic developer compositions containing such toner compositions.

Yet other objects of the instant invention will become apparent from a consideration of the specification and appended claims.

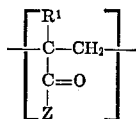
According to the present invention there is provided for use in dry developer compositions a dry electrostatic toner compositions comprising an aromatic resin with recurring units containing alternating methylene groups and aromatic groups. The methylene group may be linked directly to the ring structure of the aromatic groups or to side chains attached to the aromatic ring.

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Aromatic resins useful in the present invention include polymers containing the following recurring units:



and



wherein Z is an aromatic moiety including mono- and polynuclear aromatic ring structures and carbocyclic and heterocyclic aromatic ring structures, each structure typically containing 1 to 3 aromatic rings having 5 to 8 atoms per ring including O, S, and C atoms; R is selected from the group containing hydrogen, alkyl moieties typically containing 1 to 4 carbon atoms such as methyl, ethyl, etc., aryl moieties and aryloxy moieties typically containing 1 to 3 aromatic rings, alkoxy moieties typically containing 1 to 4 carbon atoms such as methoxy, etc., and amino moieties including alkyl and dialkyl substituted amino groups having 1 to 3 carbon atoms in the alkyl substituent; and R¹ represents hydrogen or methyl moieties.

Suitable aromatic polymers useful in the present invention typically have an inherent viscosity, N_i, in the range between about 0.01 to about 0.3. The inherent viscosity is determined at 25° C. in accordance with the following formula:

$$N_i = \ln \frac{N_{\text{solution}}}{N_{\text{solvent}}} / C$$

wherein N solution is the viscosity of the solution, N solvent is the viscosity of the solvent and C is the concentration in grams of the polymer in 100 cc. of chloroform. Preferred aromatic polymers have an inherent viscosity in the range between about 0.01 and about 0.20, as measured in a chloroform solution at a concentration of 0.25 g. of polymer per 100 ml. of solvent. The melting point of useful polymers usually is in excess of 60° C. with preferred resins having a melting point within the range of from about 65° C. to about 120° C. The melting point of the useful polymers described is determined by Fischer-Johns equipment, Fischer Scientific Catalog No. 12-144.

Representative examples of the aromatic resins useful in the present invention are shown in Table I below.

TABLE I

No.:	Resin
1 -----	Poly(benzyl).
2 -----	1-acetonaphthone-formaldehyde resin.
3 -----	Acetophenone-formaldehyde resin.
4 -----	Acenaphthene-formaldehyde resin.
5 -----	2-methoxynaphthalene-formaldehyde resin.
6 -----	Aniline-formaldehyde resin.
7 -----	Aniline-methylaniline-formaldehyde resin.
8 -----	Dibenzofuran-formaldehyde resin.
9 -----	Dibenzothiophene-formaldehyde resin.

The aromatic resins useful in forming the toner particles of the present invention can generally be prepared in one of two ways. One method is by a Friedel-Crafts self-condensation of a halomethyl-substituted aromatic compound. The other is by condensation of an aromatic compound or mixture of various different aromatic compounds with formaldehyde. Using the latter method, one may obtain some methylene ether bridges or linkages between aromatic groups. Accordingly, it will be appreciated that in the present specification and claims the phrase "an aromatic resin having recurring units containing alternating methylene groups and aromatic groups" is defined to include aromatic resins wherein some of the recurring units contain alternating methylene ether groups and aromatic

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groups, rather than methylene groups and aromatic groups. Generally, no more than about 15% of the total number of recurring units contained in a particular resin will contain methylene ether groups rather than methylene groups. When the aromatic resins are prepared by condensation of an aromatic compound(s) with formaldehyde varying amounts of these two components may be used. Generally, however, it is preferred to use an approximately equimolar ratio of formaldehyde and aromatic compound within the range of from about 0.5 to about 1.5 moles aromatic compound per mole of formaldehyde. Since both methods used to form the aromatic resins used in the invention involve well-known chemical processes, further extended discussion thereof is deemed unnecessary. Specific examples of both methods used to produce the toner materials of the invention are provided in the accompanying examples.

The toner particles of the present invention can be prepared from the above-described aromatic resins by various methods. Two convenient techniques for preparing these toners are spray-drying and melt-blending followed by grinding. Spray-drying involves dissolving the polymer and any other addenda 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 dyed resin. The ultimate particle size is determined by varying the size of the atomizing nozzle and the pressure of the gaseous atomizing agent. Conventionally, particles of a diameter between about ½ μ and about 30 μ are used.

The present toners can also be prepared by melt-blending. This technique involves melting a powdered form of polymer or resin and, if desired, mixing it with suitable colorants and additives. The resin can readily be melted on heated compounding rolls which are also useful to stir 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. The resultant toner particles usually range in size from about ½ to about 30 μ.

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 Color Index, vols. I and II, 2nd ed. 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) Fuchsine 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 copending application Ser. No. 770,122 filed Oct. 23, 1968, in the name of James R. Olson and entitled "Uniform Polarity Resin Electrostatic Toners." Carbon black also provides a useful colorant. 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 polymer. Particularly good results are obtained when the amount is from about 5 to 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 to containing the aromatic polymer and colorant, the toner particles of the present invention may, if desired, also contain a wetting agent. The wetting agent aids in promoting even, uniform contact between the toner and the paper support to which the toner image is ultimately fixed by heat. It is most advantageously used when fusing is accomplished through the use of infrared radiation, as it reproduces a uniform, high-density image otherwise difficult to obtain. The concentration of wetting agents may likewise vary over a wide range. Useful results are obtained at a concentration of from 0.1 to about 2.0 percent of the weight of the polymer, with the preferred range being from about 0.5 to about 1.5 percent.

Typical wetting agents which may be used, if desired, in preparing the toners of this invention include, for example, sodium sulfosuccinic acid bistridecyl ester, sodium di-isooctyl-succin - 1-sulfonate, p-tert-octyl phenoxy poly (ethylene oxide), alkaryl polyether alcohols, polyoxyethylene lauryl ethers, sodium salts of β -amino propionates, heterocyclic tertiary amines, and many others. Agents such as these are sold under such names as Aerosol OT, Aerosol TR, Amine C, Triton X-100, OPE-3, Tergitol 15-S3, and Atlas G3634A.

The toners of this invention can be mixed with a carrier vehicle to form developing compositions. The carrier vehicles which can be used with the present toners to form new developer compositions can be selected from a variety of materials. Suitable carriers useful in this invention include various non-magnetic particles such as glass beads, crystals of inorganic salts such as sodium or potassium chloride, hard resin particles, metal particles, etc. In addition magnetic carrier particles can be used with the toners of this invention. Suitable magnetic carrier materials are particles of ferromagnetic materials such as iron, cobalt, nickel and alloys thereof. Other magnetic carriers that can be used are resin particles coated with a thin, continuous layer of a ferromagnetic material as disclosed in Miller, Belgium Pat. 726,806 issued Mar. 14, 1969, and entitled "Metal Shell Carrier Particles." The carrier particles used typically have an average particle size between about 1200 and about 30 μ , depending on the size of the toner particles used. Preferred carriers have a particle size between about 600 and about 40 microns. Still other useful magnetic carriers are ferromagnetic particles overcoated with a thin, continuous layer of a film-forming, alkali-soluble carboxylated polymer as disclosed in Miller, U.S. Pat. 3,547,822, issued Dec. 15, 1970, and entitled "Scum-Retardant Carrier Particles and Compositions Thereof." If desired, the carrier particles may contain a particulate conductive material to alter the triboelectric properties of the particles as described in Canadian Pat. 835,317.

The weight ratio of toner to carrier can be varied over a wide range. Useful results are obtained when the developer composition contains from about 0.5 to about 15 percent by weight of toner and about 99.5 to 85 percent by weight of carrier. Preferred developers contain from about 1 to 10 percent by weight of toner and about 99 to about 90 percent by weight of carrier.

The toner and developer compositions of this invention can be used in a variety of ways to develop electrostatic charge patterns or latent images. Such developable charge patterns can be prepared by a number of means and can be carried on either an electrophotographic element or a non-sensitive element such as a receiver sheet. One suitable technique involves cascading the developer composition across the electrostatic charge pattern, while another technique involves applying toner particles from a magnetic brush. This latter technique requires the use of a magnetically attractable carrier vehicle in forming the developer composition. After imagewise deposition of the toner particles, the image can be fixed by heating the toner to cause it to fuse to the substrate carrying the toner.

If desired, the unfused image can be transferred to another support and then fused to form a permanent image.

The toners of this invention when used with a carrier as described above show greatly improved properties. Electrostatic attraction to the carrier is excellent, so there is negligible throw-off from a rapidly rotating magnetic brush of the type in common use in electrostatic copying machines. Typically, these toners have a minimum caking temperature above about 55° C. Charge uniformity is very high, as can be seen by the freedom from background toning described in the examples. There is also a high degree of freedom from scum when images are formed using the toners of the invention.

The following examples are included to illustrate further the advantages of the novel toner and developer compositions of this invention.

EXAMPLE 1

In Examples 1A-1H set forth hereinbelow there is illustrated the preparation of various aromatic resins useful in the present invention. Example 1A illustrates the use of a Friedel-Crafts self-condensation reaction of a halomethyl-substituted aromatic compound to form aromatic resins useful in the present invention. Examples 1B-1G illustrate the use of a condensation reaction between formaldehyde and a suitable aromatic compound to form aromatic resins useful in the present invention. Example 1H illustrates the preparation of a phenolformaldehyde resin used for comparative purposes in Example 2. Examples 1B and 1C illustrate aromatic resins containing a recurring unit as illustrated in Formula II hereinabove and Examples 1A and 1C-1G illustrate resins containing a recurring unit as illustrated in Formula I hereinabove.

Preparation of resins

(1A) Polybenzyl.—In an open vessel equipped with a stirrer, benzyl chloride is heated with a trace of ferric oxide until hydrogen chloride begins to evolve. When the initial vigorous reaction subsides, heating is continued until no more gas is evolved and the temperature reaches 110°. On cooling the material hardens to a glassy resin of polybenzyl. The Fisher-Johns melting point of the resin is 80-92° C.

(1B) 1-acetonaphthone-formaldehyde.—A mixture of 60 g. of 1-acetonaphthone, 37 g. of 37% aqueous formaldehyde, 3 g. of sodium hydroxide and 350 ml. of ethanol is stirred at reflux 90 minutes. During this time the resin separates. The liquid is removed by decantation, and the resin is washed by stirring it at reflux with two portions of 2:1 ethanol-water. The hardened resin is ground to a powder and soaked in ethanol-water to further wash it. The Fisher-Johns melting point of the acetonaphthone-formaldehyde resin produced is 98-107° C.

(1C) Acetophenone-formaldehyde.—The resin is made from acetophenone in a manner similar to that of resin 1B. The Fisher-Johns melting point of the acetophenone-formaldehyde produced is 66-78° C.

(1D) Acenaphthene-formaldehyde.—A mixture of 92 g. of acenaphthene, 18 g. of paraformaldehyde, 1 g. of p-toluene-sulfonic acid, 150 ml. of dioxane, 150 ml. of toluene is heated at 60° for 24 hours, then poured into isopropyl alcohol to precipitate the resin product. The Fisher-Johns melting point of the acenaphthene-formaldehyde resin produced is 90-114° C.

(1E) 2-methoxynaphthalene-formaldehyde.—This material is made from 2-methoxynaphthalene in the same manner as resin 1D. The Fisher-Johns melting point of the resin obtained is 116-122° C.

(1F) Aniline-formaldehyde.—To a mixture of 43 ml. of concentrated hydrochloric acid and 750 ml. of water is added 42 g. of aniline and 40 g. of 37% aqueous formaldehyde. The mixture is warmed at 40° for an hour then poured into a well-stirred solution of 21 g. of sodium hydroxide in one liter of water. The resin which pre-

cipitated is recovered by filtration, washed and dried. The Fisher-Johns melting point of the resin is 88–105° C.

(1G) Aniline-methylaniline-formaldehyde.—This resin is made in the same manner as resin 1F substituting N-methyl-aniline for half of the aniline. The Fisher-Johns melting point of the resin is 83–92° C.

(1H) Phenol-formaldehyde.—A mixture of 130 g. phenol, 100 g. 37% formaldehyde, 13 ml. water and 1.5 ml. concentrated hydrochloric acid is stirred at reflux for 1½ hours. The molten resin which forms is washed by stirring it with two 400 ml. portions of boiling water. The water is removed by decantation and the resin is dried by vacuum at 190° C. The Fisher-Johns melting point of the resin is 72–85° C.

EXAMPLE 2

Each of resins 1A–1H is used to prepare a toner and a developer composition in the following examples, 2A–2H. 2A–2G illustrate toners and developers of the present invention whereas 2H is a prior art toner and developer included for comparative purposes. Electrophotographic prints are made using each developer and examined to determine the amount of background deposit, charge uniformity, density, and ease of transfer.

Preparation of toner and developer

The following general procedure is used to prepare a xerographic toner from each of the resins. The polymer is melted on compounding rolls at the indicated melt temperature or heating oil temperature and held at this temperature for about 20 minutes to obtain a uniform melt. The colorants are added and blended by passing the melt through the space between the rolls five times. The melt is cooled, coarse ground to pass a 20 mesh screen, and finally ground in a fluid energy mill at about 30 p.s.i.g. to a maximum particle size of 25 μ . Developers prepared from each of the toners illustrated in 2A–2H contain 3 g. of toner in admixture with 97 g. of Glidden 388 plastiron particles as a particulate carrier. The electrophotographic prints obtained in Examples 2A–2G are prepared by charging an organic photoconductive plate negatively, exposing the charged plate to a positive-appearing image pattern of actinic radiation, and developing the resultant electrostatic charge image on the plate by means of a hand magnetic brush containing the toner-carrier mixtures of 2A–2G. The imagewise toner deposit on the plate is then transferred to bond paper by application of a negative potential and fixed on the paper by heating the paper a few seconds on a hot plate. Example 2H illustrating the use of the phenol-formaldehyde toner, is similar to Examples 2A–2G except the phenol-formaldehyde toner particles, contrary to the toner particles of Examples 2A–2G appear to exhibit a predominantly negative charge with respect to the plastiron carrier particles. Hence, in Example 2H the organic photoconductor-containing plate is given an initial negative charge, then exposed to a positive-appearing image pattern of actinic radiation, developed, and transferred to obtain a resultant electrophotographic print. The specific formulation of each toner and the result obtained when each is used to prepare an electrophotographic print are presented below:

EXAMPLE 2A

Toner prepared from resin of Ex. 1A

A toner is prepared from resin 1A at a melt temperature of 100° C. having the following composition:

- 50 g. polymer 1A
- 1.76 g. docosanoic acid
- 2.25 g. nigrosine base, C.I. No. 50415B (2.28 meq./g. solid)
- 2.5 g. each of color balancing dyes 1,4-dihydroxy-5,8-bis-(4-methylanilino)-9,10-anthraquinone and 4-(4-methyl-2-nitrophenylazo)-5-methyl-3-pyrazolone
- 2.85 g. Carbon Black Sterling FT (Cabot).

A developer containing 3 g. toner and 97 g. Glidden 388 plastiron is mixed by shaking in a glass bottle. Toner shows excellent adherence to iron carriers. An electrophotographic print is prepared using this developer by charging organic photoconductor-containing plate negatively, exposing to a photographic positive, and developing with a hand held magnetic brush at bias potential of about –50 v. Toner is deposited in unexposed areas and exhibits good uniformity of charge (no negatively charged particles are detected). Transfer to paper is nearly complete. Image is fixed by placing paper, toned side up, on a hot plate at 150° C. for a few seconds. Image density and sharpness are good.

EXAMPLE 2B

Toner prepared from resin 1B

A toner is prepared from resin 1B at a melt temperature of 115° C. having the following composition:

- 80 g. polymer 1B
- 2.84 g. docosanoic acid
- 3.6 g. nigrosine base (same as in Example 2A)
- 0.4 g. each of 1,4-dihydroxy-5,8-bis(4-methylanilino)-9,10-anthraquinone and 4-(4-methyl-2-nitrophenylazo)-5-methyl-3-pyrazolone
- 4.56 g. Carbon Black Sterling FT.

A developer is prepared and print made as in Example 2A. Toner shows uniform positive charge (no negative particles are detected); image sharpness and density are good.

EXAMPLE 2C

A toner is prepared from resin 1C at a melt temperature of 83° C. having the following composition:

- 100 g. polymer 1C
- 3.55 g. docosanoic acid
- 4.75 nigrosine base (same as in Example 2A)
- .5 g. each of 1,4-dihydroxy-5,8-bis(4-methylanilino)-9,10-anthraquinone and 4-(4-methyl-2-nitrophenylazo)-5-methyl-3-pyrazolone
- 5.7 g. Sterling FT Carbon Black.

Developer is prepared and tested as in Example 2A. Toner shows uniform positive polarity (no negative polarity particles are detected). Prints show some brush marks and image smearing. Density is good.

EXAMPLE 2D

A toner is prepared from 1D at a melt temperature of 111° C. having the following composition:

- 90 g. polymer 1D
- 3.19 g. docosanoic acid
- 4.05 g. nigrosine base (same as in Example 2A)
- .45 g. each of 1,4-dihydroxy-5,8-bis(4-methylanilino)-9,10-anthraquinone and 4-(4-methyl-2-nitrophenylazo)-5-methyl-3-pyrazolone
- 5.12 g. Carbon Black Sterling FT.

Developer is prepared and tested as in Example 2A. Toner shows uniform positive polarity (no negative particles are detected). Image sharpness is good, density is fair with little evidence of brush marks in image areas.

EXAMPLE 2E

A toner is prepared from resin 1E at a melt temperature of 128° C. having the following composition:

- 80 g. polymer 1E
- 2.84 g. docosanoic acid
- 3.6 g. nigrosine base (same as in Example 2A)
- 0.4 g. each of 1,4-dihydroxy-5,8-bis(4-methylanilino)-9,10-anthraquinone and 4-(4-methyl-2-nitrophenylazo)-5-methyl-3-pyrazolone
- 4.56 Carbon Black Sterling FT.

Developer is prepared and tested as in Example 2A. Toner shows good uniform positive polarity (no negative particles are detected). Image sharpness and density are good with no evidence of brush marks.

EXAMPLE 2F

A toner is prepared from resin 1F at a heating oil temperature of 160° C. having the following composition:

- 40 g. polymer 1F
1.8 g. nigrosine base, C.I. No. 50415B (2.28 meq. base/g. solid)
2.18 g. stearic acid
0.2 g. of 1,4-dihydroxy-5,8-bis(4-methylanilino)-9,10-anthraquinone and 4-(4-methyl-2-nitrophenylazo)-5-methyl-3-pyrazolone.

Developer is prepared and tested as in Example 2A. The toner shows excellent adherence to the iron surface, and uniform positive polarity (no negative particles are detected). Image sharpness and density are very good, no brush marks in image. Transfer from photoconductor is nearly complete.

EXAMPLE 2G

A toner is prepared from resin 1G at a heating oil temperature of 132° C. having the following composition:

- 50 g. polymer 1G
2.25 g. nigrosine base (same as in Example 2F)
2.7 g. stearic acid
0.25 g. each of 1,4-dihydroxy-5,8-bis(4-methylanilino)-9,10-anthraquinone and 4-(4-methyl-2-nitrophenylazo)-5-methyl-3-pyrazolone.

Developer is prepared and tested as in Example 2A. Image density and sharpness are good with some evidence of brush marks in image areas. The toner exhibits uniform positive polarity. Transfer to paper is nearly complete.

EXAMPLE 2H

To illustrate the difference in charge polarity characteristics between toners of the prior art prepared from phenol-formaldehyde resin and toners of the present invention, a toner composition is prepared using resin 1H at a heating oil temperature of 137° C. having the following composition:

- 50 g. polymer 1H
2.25 g. nigrosine base C.I. 50415B (same as in Ex. 2F)
2.73 g. stearic acid
0.25 g. each of 1,4-dihydroxy-5,8-bis(4-methylanilino)-9,10-anthraquinone and 4-(4-methyl-2-nitrophenylazo)-5-methyl-3-pyrazolone
3.0 g. Sterling 10R Carbon Black (Cabot).

A developer is prepared as in Example 2A. Toner particles of the developer exhibit both positive and negative polarity with respect to iron carriers although the particles of negative polarity appear to predominate. An electrographic print is prepared by charging a photoconductive element negatively, applying a negative bias to the magnetic brush, exposing to a positive-appearing image pattern of actinic radiation, and transferring with a negative corona potential to produce a resultant positive electrophotographic print. A positive corona potential is then applied to the same photoconductive element with the result that toner particles are removed from background areas of the element, thereby indicating the presence of both positive and negative polarity toner particles in the developer.

In addition to phenol-formaldehyde resin other hydroxy-substituted aromatic-formaldehyde resins, including p-phenylphenol-formaldehyde resin and p-cresol-formaldehyde resin, are tested and also exhibit bicharging, i.e., toner particles prepared from these resins exhibit both positive and negative polarity, with respect to iron carrier particles.

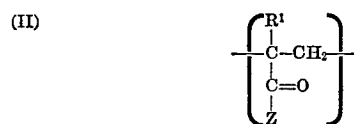
The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

We claim:

1. A dry developer composition for use in developing electrostatic charge patterns comprising a triboelectric mixture of particulate carrier vehicle and finely-divided electroscopic toner particles having an electrostatic polarity opposite that of said vehicle, said toner particles comprising a thermoplastic aromatic resin containing recurring units having alternating methylene and aromatic groups, such units having either of the following formulas:



and



wherein Z represents an aromatic ring structure free from hydroxy substituents and containing 1 to about 3 aromatic rings; R is selected from the group consisting of hydrogen, alkyl moieties having 1 to 4 carbon atoms, aryl moieties having 1 to about 3 aromatic rings, aryloxy moieties having 1 to about 3 aromatic rings, alkoxy moieties having 1 to 4 carbon atoms, and amino moieties; and R¹ represents a hydrogen or methyl group.

2. A developer composition as described in claim 1 wherein said thermoplastic resin has an inherent viscosity of from about 0.01 to 0.3.

3. A developer composition as described in claim 1 wherein said toner particles have incorporated therein a colorant.

4. A developer composition as described in claim 1 wherein said toner particles have incorporated therein carbon black.

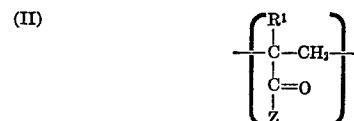
5. A developer composition as described in claim 1 wherein said aromatic resin is selected from the group consisting of polybenzyl resin, acetonephthalone-formaldehyde resin, acetophenone-formaldehyde resin, acenaphthene-formaldehyde resin, methoxynaphthalene-formaldehyde resin, aniline-formaldehyde resin, and aniline-methylaniline-formaldehyde resin.

6. A developer composition as described in claim 1 wherein said finely-divided toner particles have an average diameter of about 1/2 to about 30 microns.

7. A dry developer composition comprising triboelectric mixture of carrier particles having an average diameter of from about 30 to about 1200 microns and finely-divided electroscopic toner particles having an electrostatic polarity opposite that of said carrier particles and having an average diameter of about 1/2 to about 30 microns and comprising (a) a colorant in an amount of from about 3 to about 20 percent by weight of said particles, and (b) a thermoplastic aromatic copolymer of an aromatic compound and formaldehyde, said copolymer containing recurring units having a formula selected from the group:



and



75 wherein Z represents an aromatic ring structure free

from hydroxy substituents and containing 1 to about 3 aromatic rings; R is selected from the group consisting of hydrogen, alkyl moieties having 1 to 4 carbon atoms, aryl moieties having 1 to about 3 aromatic rings, aryloxy moieties having 1 to about 3 aromatic rings, alkoxy moieties having 1 to 4 carbon atoms, and amino moieties; and R¹ represents a hydrogen or methyl group, said copolymer having a melting point in excess of 60° C.

8. A dry developer composition as described in claim 7 comprising about 0.5 to about 15 percent by weight of toner particles and about 99.5 to about 85 percent by weight of carrier particles.

9. A developer composition as described in claim 7 wherein said carrier particles comprises ferromagnetic particles.

10. A dry developer composition comprising a triboelectric mixture of about 90 to about 99 percent by weight magnetic carrier particles having an average diameter of from 30 to about 1200 microns and about 10 to about 1 percent by weight of finely-divided electroscopic toner particles having an electrostatic polarity opposite that of said carrier particles and having an average diameter of about 1/2 to about 30 microns and comprising (a) a colorant in an amount of from about 3 to about 20 percent by weight of said particles, and (b) a thermoplastic aromatic copolymer of an aromatic compound and formaldehyde, said copolymer containing recurring units having a formula selected from the group:



and



wherein Z represents an aromatic ring structure free from hydroxy substituents and containing 1 to about 3 aromatic rings; R is selected from the group consisting of hydrogen, alkyl moieties having 1 to 4 carbon atoms, aryl moieties having 1 to about 3 aromatic rings, aryloxy moieties having 1 to about 3 aromatic rings, alkoxy moieties having 1 to 4 carbon atoms, and amino moieties; and R¹ represents a hydrogen or methyl group, said polymer having a melting point in excess of 60° C.

11. A developer composition as described in claim 10 wherein said aromatic resin is selected from the group consisting of acetophenone-formaldehyde resin, acetophenone-formaldehyde resin, acenaphthene-formaldehyde resin, methoxynaphthalene-formaldehyde resin, aniline-formaldehyde resin, and aniline-methylaniline-formaldehyde resin.

12. In an electrostatic image-forming process wherein an electrostatic image pattern carried on a support is developed by contacting such pattern with dry, finely-divided, electroscopic toner particles, the improvement wherein said particles comprise a thermoplastic aromatic resin containing recurring units having either of the following formulas:



and



25 wherein Z represents an aromatic ring structure free from hydroxy substituents and containing 1 to about 3 aromatic rings; R is selected from the group consisting of hydrogen, alkyl moieties having 1 to 4 carbon atoms, aryl moieties having 1 to about 3 aromatic rings, aryloxy moieties having 1 to about 3 aromatic rings, alkoxy moieties having 1 to 4 carbon atoms, and amino moieties; and R¹ represents a hydrogen or methyl group.

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NORMAN G. TORCHIN, Primary Examiner

J. P. BRAMMER, Assistant Examiner

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,809,554 Dated May 7, 1974

Inventor(s) Stewart H. Merrill and James R. Olson

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 6, line 45, "1-acetonaphthrone-" should read
-- 1-acetonaphthone- --.

Column 6, line 61, after "dioxane," insert --and--.

Column 8, line 73, "nitrophenzyl-" should read
-- nitrophenyl- --.

Column 10, line 53, after "comprising" insert --a--.

Column 11, in formula (II), the portion reading

C-O should read C=O

Signed and sealed this 17th day of September 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents