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(71) Applicant: **XEROX CORPORATION, Xerox Square - 020, Rochester New York 14644 (US)**

(72) Inventor: **Ims, Dale R., 926 Little Pond Way, Webster New York (US)**
Inventor: **Knapp, John F., 38 Lambeth Loop, Fairport New York (US)**
Inventor: **Bolte, Steven B., 26 Maryvale Drive, Webster New York (US)**
Inventor: **Lewis, Richard B., 1262 Salmon Creek Road, Williamson New York (US)**

(74) Representative: **Goode, Ian R. et al, European Patent Attorney c/o Rank Xerox Limited,Patent Dept. Rank Xerox House 338 Euston Road, London NW1 3BH (GB)**

(54) **Electrostatographic toner composition and developer composition comprising the same.**

(57) An electrostatographic toner composition comprising a colorant and a blend of a lower alkanoic acid esterified epoxy resing and a lower alkanoic acid esterified phenoxy resin, the ratio by weight of the epoxy resin to phenoxy resin being between 1 to 4 and 4 to 1. The epoxy resin and the phenoxy resin may be obtained from the reaction products of an epihalohydrin and a dihydric alcohol, the alkanoic acid ester being a acetic acid ester.

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ELECTROSTATOGRAPHIC TONER COMPOSITION

This invention relates to an electrostatographic toner composition comprising a colorant and a blend of resins.

In the development of electrostatographic images, a toner composition is mixed with a carrier composition in order to impart the proper charge characteristics to the toner particles and also for the purpose of carrying the toner particles by a physical means to the surface which contains the latent electrostatic image. The carrier particles are generally much larger in particle size than that of the toner varying from perhaps 50 to 100 times larger depending upon the particular developer being employed. The toner is thus subjected to large forces in the development housing and in transit toward the imaging surface, which forces result in the particle size reduction of the toner particles. This creates problems because it not only provides a source for dirt made up of the fine toner particles but also changes the triboelectric character of the toner particles because of the reduction in size thereof and the impaction and adhesion to the carrier particles. On the other hand, for economic reasons it is desired to use customary particle size reduction techniques to achieve the desired particle size of the colorant filled resinous materials. Uniformity in particle size can be achieved subsequent to size reduction by standard classification methods. A problem encountered because of these objectives is that particle size reduction will also occur in the electrostatographic apparatus because the conditions therein are similar

to that encountered in the size reduction apparatus. Thus, brittle failure of the toner particles together with size reduction occurs in the electrostatographic process. This size reduction during the electrostatographic process results in changes in both the triboelectric and charging characteristics of the toner particles with respect to the particular carrier materials employed in the process. That is, as the particle size reduction of the toner particles occurs, the charge to mass ratio on the particles increases thereby increasing the forces holding the size reduced toner particles to the carrier particles. This results in even more harsh impacts between the large size carrier particles and the toner particles either causing further reduction in the particle size or flattening of the particles out in a pancake fashion which tightly adhere to the surface of the carrier particles eventually resulting in reduction in the triboelectric characteristics.

In the prior art, namely U.S. Patent 3,393,229, issued July 16, 1968, and U.S. 4,097,620, issued June 27, 1978, there is described the use of polyethers as prepolymers and the use of resins for preparing toners and more specifically modified epoxy resins, reference column 8, line 4, of U.S. 4,097,620. These two references are merely representative of some of the prior art in this area of technology.

The toner composition of the present invention is intended to have improved and long-lasting mechanical and electrical properties, and is characterised in that the resin blend is a lower alkyl esterified epoxy resin and a lower alkyl esterified phenoxy resin, wherein the ratio by weight of the epoxy resin to the phenoxy resin is between 1 to 4 and 4 to 1.

Such blends exhibit extraordinary toughness and long life in the development of electrostatic latent images while at the same time offer extremely

good fusing characteristics and excellent blocking characteristics during storage, shipping and in the development procedure of the electrostatographic machine.

The colorant is employed in an amount of from about 5 to 15 percent based on the weight of the resin employed. The weight ratio of the epoxy resin to the phenoxy resin is preferably from about 1:2 to about 2:1 and most preferably in the ratio of about 1:1.

Both the epoxy resins and the phenoxy resins are commercially available materials prepared by reacting an epihalohydrin such as epichlorohydrin with a dihydricphenol such as for example, bis-(p-hydroxyphenyl)-methane, bis-(p-hydroxyphenyl)-dimethyl methane, (bisphenol A), bis-(p-hydroxyphenyl)-methylphenyl methane, bis-(p-hydroxyphenyl)-tolylmethane, 4,4'-dihydroxydiphenyl, bis-(p-hydroxyphenyl)-sulfone, resorcinol, catechol, hydroquinone and the like. Suitable epoxy resins employed herein are those having a weight average molecular weight of from about 10,000 to about 25,000 and preferably from about 15,000 to about 22,000. The phenoxy resins employed herein have a weight average molecular weight of from about 40,000 to about 60,000. The molecular weights are measured by Gel Permeation Chromatography. As indicated above, these materials are commercially available.

In the esterification of the epoxy and phenoxy resins, the two types of materials may be separately esterified and then combined in the ratios desired or the epoxy resin and the phenoxy resin may be mixed together and esterified simultaneously. In the esterification procedure, any suitable lower alkyl esterifying agent such as, for example, acetic acid, acetyl chloride, acetic anhydride, propionic acid, propionic anhydride, propionyl chloride, butyric acid, butyroyl chloride, butyric anhydride, valeric acid, valeric anhydride, valeryl chloride and the like may be used. Either

the same or different esterifying agents can be employed should the procedure for esterification be the separate technique mentioned above wherein the phenoxy and the epoxy resins are each severally esterified. A particularly useful resin is an acetylated blend of 50 weight percent Epon 1010 sold by Shell Chemical Company and Phenoxy PKHC sold by Union Carbide Corporation.

In the process for the esterification of the epoxy and/or the phenoxy resin, the esterifying agent, such as acetic anhydride is reacted in an excess amount with the particular resin or blend of resins with heating and agitation in a suitable solvent such as, for example, toluene, benzene, xylene or the like. The agitation is continued for a period of hours at a suitable temperature such as 80 to 130°C. The course of the reaction can be determined by IR spectra of the polymer which is precipitated and washed to remove the acetic acid and acetic anhydride. As the reaction progresses, the OH peak at about 3500 cm^{-1} disappears and the carbonyl peak at about 1750 cm^{-1} grows.

The acetylated polymer product can be separated from the reactants and by products by the addition of an excess of ethanol at a temperature of between 70 and 75°C with agitation for two or three hours. A distillation is then conducted, the excess ethanol and ethyl acetate, formed by reaction with the excess acetic anhydride being removed at a temperature of about 76 to 78°C and the acetic acids/toluene azeotrop comes off at a temperature of 105.6°C. Continued distillation produces toluene at about 110°C. The polymer can then be drawn off and stored.

In the practice of this invention, any suitable blend of esterified polymers as described above may be used in the preparation of toner particles by combining with a suitable colorant. The toner may be prepared by dissolving the resinous material and a coloring agent such as a dye or a pigment or by dissolving the resin and dispersing the colorant, should it be insoluble,

in a suitable solvent and spray drying to achieve uniformly sized toner particles. The toner size may vary from about 1 micron to about 20 microns and preferably from about 10 to about 15 microns. The toner particles should be of substantially uniform size because of the nature of the spray drying operation.

In the preparation of the toner material, any suitable colorant may be employed such as, for example, pigments or dyes including, carbon black, nigrosine dye, aniline blue, Calco Oil Blue, chrome yellow, Ultramarine blue, DuPont Oil Red, Quinoline Yellow, methylene blue chloride, phthalocyanine blue, Malachite Green Oxylate, lamp black, Rose Bengal and other pigments and dyes set forth in the Color Index, Vols. I and II, Second Edition. Should a magnetic toner be desired, the colorant may be a magnetic material such as iron particles, iron oxide, nickel, ferrite, magnetite or mixtures of magnetic particles and colorant.

In the preparation for spray drying, the resinous material employed and the colorant is dissolved in any suitable solvent such as, for example, chlorinated solvents including trichloroethane, methylene chloride, tetrachlorethane, methylene dichloride, chloroform, aromatic solvents such as toluene, benzene, naphthalene, xylene, ketones such as, for example, methylethyl ketone, acetone, esters such as ethylacetate, amylacetate, mixtures thereof and the like. The solvent should be chosen in order to assure that all the resin components are soluble.

The spray drying operation may be conducted in a suitable spray drying apparatus such as, for example, the Bowen Laboratory spray dryer manufactured by Bowen Engineering Corporation, North Branch, New Jersey. This unit is a lab size conical dryer with concurrent airflow and has an interchangable atomizing head mounted near the top of the drying chamber. Any suitable atomizing

head may be employed such as, rotating disks, high pressure nozzles, and the like. In order to achieve uniformity in size of the particles, it may be desirable to classify the particles by any suitable classification techniques well known in the classification art.

The toners of this invention can be mixed with a suitable carrier to form electrostatographic developers. Any suitable carriers having a particle size of from about 30 microns to about 1,000 microns may be employed such as, for example, glass beads, sand, particles of ferromagnetic materials such as iron, cobalt, nickel, alloys thereof, ferrites, and the like. Resinous materials such as methylmethacrylate, styrene and any suitable resinous materials in particle sizes set forth above. The carriers may be employed with or without a coating. Many suitable resinous coating materials may be employed such as polyolefins, such as polyethylene polymethylstyrene, polymethylmethacrylate, polyacrylonitrile, polyvinylacetate polyvinyl alcohol, polyvinyl carbazole, fluorocarbons, such as polytetrafluorethylene, polyvinylidene fluoride, polyamides, polyurethanes, polycarbonates and the polymers set forth in U.S. Patent 3,526,533. Many of the foregoing and other typical carriers are described in U.S. Patent Numbers 2,638,416; 2,618,552 and 4,075,391. It is preferred that the carrier be chosen in order that the charge to mass ratio of the blown-off toner is from about 10 to about 40 microcoulombs/gram and preferably from about 10 to 30 microcoulombs/gm. The method of measuring charge to mass ratio is set forth in U.S. Patent 3,533,835.

The toner composition generally comprises from about 0.1 to about 15 percent by weight of the total toner carrier weight. Preferably, the toner is present in an amount of from about 0.5 to 5 percent by weight based on the total weight of the developer mixture.

In addition to the presence of toner and carrier, because the toner particles are prepared by spray drying, it is generally preferred to add a flow agent to the developing mixture in order to obtain the optimum flow characteristics of the toner in the electrostatographic system. Any suitable flow agent such as, for example, colloidal silica, aluminum oxide, titanium dioxide, talc and the like may be employed. These flow aids are sub-micron in size and preferably from about 50Å to about 500Å. The flow agents are added in an amount of from about 0.05 to about 1% based on the weight of the toner, and preferably from about 0.1 to about 0.5%.

The invention is further illustrated by the following example in which parts and percentages are by weight unless otherwise specified.

Example I

About 50 parts of a polyglycidyl ether prepared from epichlorohydrin and bisphenol A having a weight average molecular weight of about 20,000, a Tg of about 87°C, obtained by differential scanning calorimeter, and a Durran Melting Point of about 160°C, sold as Epon 1010 by Shell Chemical Company and about 50 parts of a phenoxy resin prepared from epichlorohydrin and bisphenol A having a Tg of 100°C, an ultimate compressive stress of 703 to 843 kg/cm^2, a tensile yield stress of 633 kg/cm^2, a maximum elongation of 50%, a compression modulus of $2.25 - 2.4 \times 10^4$ kg/cm^2, a tensile modulus of $2.4 - 2.7 \times 10^4$ kg/cm^2 and a density of 1.17 gm/cm^3 obtained from Union Carbide Corporation under the name PKHC are charged to a flask equipped with a condenser, a heating mantle and a stirring rod together with about 200 parts of toluene and about 120 percent excess of acetic anhydride. The reaction is conducted with agitation at about 100°C for about

four hours. The progress of the reaction is monitored by infrared spectra on the polymer which is precipitated from solution and washed to remove acetic acid and acetic anhydride. The OH peak at about 3500 cm^{-1} disappears and the carbonyl peak at about 1750 cm^{-1} grows as the reaction proceeds. When the reaction is completed, as evidenced by the absence of OH groups, the excess acetic anhydride is removed by reaction with an excess of ethanol for about three hours at 70 - 75°C. The ethanol and ethyl acetate are then distilled off at about 76-78°C and the acetic acid, as the azeotrope with toluene at about 106°C.

The completed acetylated blend of polyglycidyl ether and polyphenoxy, which has a Tg of about 62°C, is separated from the remaining toluene by precipitation and dissolved in chloroform from which the blend is spray dried in a Bowen Engineering spray drying apparatus to prepare resin particles of from 10 -15 microns. When sprinkled on a glass slide and placed in an oven preheated to 135°C for two minutes, the particles coalesce.

Toner particles are prepared by spray drying in the same apparatus mentioned above from a chloroform solution, the acetylated polymer blend prepared as above, the solution having about 10% carbon black dispersed therein. The toner particles have a number average particle size of about 7 microns and a volume average particle size of about 11 microns.

The toner particles are mixed with 0.1 percent of powdered aluminum oxide, as a flow aid, and this mixture then combined in an amount of 1 percent with a carrier made up on 100 micron ferrite particles prepared in accordance with Example III of U.S. Patent 4,075,391, coated in a Wurster Spouting Fluidized Bed manufactured by Dairy Equipment Company, Madison, Wisconsin, with 1.2 percent, based on the weight of the ferrite, of a copolymer of about 48 mol percent chlorotrifluoroethylene

and about 52 mol percent vinyl chloride sold by Firestone Plastics Company under the designation FPC-461, the coating containing 25% acetylene black.

This developer is used in an electrostatographic copier having a magnetic brush development assembly. After 100,000 copies no change is visible in copy quality or in the character of the toner particles when viewed under a scanning electron microscope.

Example II

The procedure of Example I is repeated except that the polyglycidyl ether and the phenoxy resin of Example I are each separately acetylated using proportionate quantities of the ingredients. The resulting esterified products are prepared into toner and mixed together in a ratio of 50% of each by weight. Substantially no difference is seen in the use of this material in an electrostatographic copier.

Example III

The procedure according to Example I is repeated except that a 120% excess of propionic anhydride is substituted for the acetic anhydride. The toner thus prepared exhibits a long developer life.

CLAIMS:

1. An electrostatographic toner composition comprising a colorant and a blend of resins, characterized in that the resin blend is a lower alkyl esterified epoxy resin and a lower alkyl esterified phenoxy resin, wherein the ratio by weight of the epoxy resin to the phenoxy resin is between about 1 to 4 and 4 to 1.

2. A toner composition in accordance with Claim 1 wherein the epoxy resin has a weight average molecular weight of from 10,000 to 30,000, and the phenoxy resin has a weight average molecular weight of from 40,000 to 60,000.

3. A toner composition in accordance with Claim 1 or Claim 2 wherein the epoxy resin and phenoxy resin are present in a weight ratio of 1:1, and the alkyl group contains from 1 carbon atom to 4 carbon atoms.

4. A toner composition in accordance with any one of Claims 1 to 3 wherein the epoxy resin has a weight average molecular weight of about 20,000 and a second order glass transition temperature of about 87°C, and the phenoxy resin has a weight average molecular weight of about 45,000 and a second order glass transition temperature of about 100°C.

5. A toner composition in accordance with any one of Claims 1 to 4 wherein the epoxy resin and the phenoxy resin are obtained from the reaction products of an epihalohydrin and a dihydric alcohol and the alkyl ester is a methyl ester.

6. A toner composition in accordance with Claim 5 wherein the dihydric phenol is bisphenol A and the epihalohydrin is epichlorohydrin.

7. A developer composition comprising the toner composition of any one of Claims 1 to 6 and a carrier material.

8. A developer composition in accordance with Claim 7 wherein the carrier material comprises ferrite particles coated with a copolymer of chlorotrifluoroethylene and vinyl chloride.

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EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
D	US - A - 4 097 620 (CHIN H.LU) + Column 6 + -- DE - B2 - 2 026 390 (FUJI) + Claims 1,2 + -- US - A - 4 022 738 (SHIMADA) + Claims 1,6 + ----	1 1 1

CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)

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TECHNICAL FIELDS SEARCHED (Int.Cl. 3)

G 03 G

CATEGORY OF CITED DOCUMENTS

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

&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	29-09-1980	SALTEN

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