(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 022 639**
A1

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **80302229.2**

(22) Date of filing: **02.07.80**

(51) Int. Cl.³: **G 03 G 9/08**, C 08 L 27/06

(30) Priority: **02.07.79 US 54191**

(43) Date of publication of application: **21.01.81**
Bulletin 81/3

(84) Designated Contracting States: **DE GB NL**

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(54) Electrostatographic toner composition and electrostatographic developer composition.

(57) An electrostatographic toner composition comprising a colorant and a copolymer of from about 65 mol percent to about 75 mol percent vinyl chloride and from about 25 mol percent to about 35 mol percent of a lower alkyl maleate or fumarate, the copolymer having a number average molecular weight of from about 15,000 to about 25,000 and a weight average molecular weight of from about 45,000 to about 55,000.

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TITLE MODIFIED see front page

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ELECTROSTATOGRAPHIC TONER COMPOSITION

This invention relates to an electrostatographic toner composition comprising a colorant and a resin.

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 5 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 sizes 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.

Representative prior art patents include U.S. 3,391,082, issued July 2, 1969, U.S. 3,941,898, June 20, 1967, and U.S. 3,965,021, issued June 20, 1967. For example US 3391082 discloses a xerographic toner wherein the resin has a second order glass transition temperature of 30° to 65°C and a limiting viscosity of 0.15 to 0.35, while US 3941898 patent teaches the preparation of a xerographic developer wherein the toner is a cross-linked polymer of a controlled molecular weight prepared by polymerizing in the presence of a cross-linking agent a material capable of controlling the molecular weight. US 3965021 is directed to a toner wherein the resinous material is a blend of at least two polymers the first having a glass transition temperature of -20°C and the second having a glass transition temperature of at least 5°C lower than that of the first polymer.

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 is a copolymer of vinyl chloride present in an amount of from 65 to 75 mole percent, and a lower alkyl maleate of fumarate, present in an amount of from 25 to 35 mole percent, which copolymer has an average number molecular weight of from 15,000 to 25,000 and a weight average molecular weight of from 45,000 to 55,000. The molecular weights enumerated are determined by Gel Permeation Chromatography.

These particular copolymers exhibit extraordinary toughness and long life in the development of electrostatic latent images and 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 two weight percent to about 15 weight percent, based on the weight of the toner and preferably from about four percent to about ten percent. A particular advantage achieved using the vinyl polymer in accordance with this invention is that sharp, dark images are obtained using 5 percent by weight carbon black which is only about one-half the amount used in commercially available compositions.

In the practice of this invention, any suitable vinyl chloride - lower alkyl maleate or lower alkyl fumarate copolymer in the quantities set forth above, may be used in the preparation of the copolymer such as, for example, the C_2 to C_4 esters of maleic acid and fumaric acid such as ethyl, diethyl, propyl, isopropyl, dipropyl, diisopropyl, butyl, isobutyl, tertiary butyl, dibutyl diisobutyl, ditertiary butyl and the like. Ethyl maleate and diethyl maleate are the preferred monomers for copolymerization with vinyl chloride.

The copolymers used in the preparation of toner compositions in accordance with this invention are generally prepared by suspension polymerization techniques which are well known in the art. In this method, the monomers are mixed together with a suitable catalyst, such as benzoyl peroxide, lauroyl peroxide, azoisobutyrylnitrile and the like and dispersed with agitation as droplets (discontinuous phase) in an aqueous medium (continuous phase) which contains stabilizers, emulsifiers and the like.

The polymer should have a suitable molecular weight such that when toner size particles are prepared, they will have sufficient toughness to withstand the vigorous environment within an electrostatographic apparatus, and at the same time exhibit the rheological properties that prevent blocking under storage and transport conditions but can be readily fixed to paper substrates by normal fusing conditions.

The toughness of the toner size particles can readily be determined by simulating conditions in an electrostatographic machine. This can be done in a roll mill wherein the resin powder is rolled with a carrier material over a period of time and by visual observation of the toner particles under a scanning electron microscope.

The blocking characteristics of the resin can be determined by measurement of the second order glass transition temperature. This generally should be as high as possible without interfering with the fusing requirements. This second order glass transition temperature should preferably be from about 41 to 65°C and preferably from about 54°C to about 63°C at a heating rate of 10°C per minute in a Differential Scanning Calorimeter.

The fusing characteristics can be determined simply by placing particles of the toner size, using particles on a glass slide, in an oven preheated to 135°C for two minutes. The particles, if satisfactory for toner, will coalesce within this time.

In a specific test for toughness of the resin, six grams of resin powder made up of resin particles having a size of from about 10 to 15 micron are rolled in a glass jar of 473 cubic centimeters at a rate of 27.5 linear meters per minute with 500 grams of 250 micron coated glass beads having a density of about 4.2 grams per cubic centimeter, which are uniformly coated to a thickness of from 0.25 to 1 micron with a copolymer of about 48 mol percent chlorotrifluoroethylene and about 52 mol percent of vinyl chloride sold by Firestone Plastics Company under the designation FPC461. Samples are withdrawn periodically and the resin powder is blown off the coated glass beads with an airstream at a pressure of 4.57 kilograms per cubic centimeter.

The blown off powder is viewed under a scanning electron microscope and a comparison is made with the original particles. The longer the rolling test can be conducted without a difference being observed, the tougher is the resin. That is, one viewing the resin particles after the rolling test should be unable to detect any substantial number of particles which have cracks or have been reduced in particle size because

of brittle failure caused by impaction with the high density glass beads.

The rolling test, set forth above can also be used in conjunction with a test for resin powder concentration and charge to mass ratio. In this test, the rolled resin particles and carrier particles are placed in a Faraday Cage and dry compressed air is blown through the cage under a pressure of 4.57 kg/cm^2 in order to remove all of the resin particles capable of being removed from the coated glass beads. A Faraday Cage is a device which consists of a brass cylinder having a diameter of 2.54 cm and a length of 2.54 cm. A 100 mesh screen is positioned at each end of the cylinder. The cylinder is weighed, charged with 0.5 grams of the above stated mixture and connected to ground through a capacitor and an electrometer connected in parallel. In addition to the determination of the resin concentration or the weight loss by impaction on the glass carrier beads, this device also is used to determine the charge on the particles in microcoulombs per gram of resin powder. The weight loss of the resin sample can occur by two modes of resin particle failure, either of which will be determined by the tests set forth above. First, the particles can fail by brittle fracture, thereby causing the attrition of the resin particles with the accompanying reduction in the mass of the resulting particles. This reduction in mass corresponds to an increase in the charge to mass ratio, thereby increasing the attractive forces between the coated glass beads and the size reduced resin particles. As the charge to mass ratio on the resin powder particles increases above 40 microcoulombs per gram, the attractive forces between the particles become so great that the resin particles and the glass bead particles become inseparable due to the action of the high pressure air passed through the Faraday Cage.

Secondly, the resin particles can fail because of ductile deformation. In this mode of failure, the resin particles become flattened against the surface of the larger high density glass beads in a pancake type formation. In such action, the particles literally become welded to the surface of the glass beads thus preventing blowoff and recovery of the toner particles. It can be seen that the tests indicated above, that is, the visual observation of the toner particles by scanning electron microscope and also the measurement of the recoverable toner after blowoff gives a precise test for determining whether a resin material will have the proper physical characteristics to withstand the forces involved in the normal operation of an electrostatographic apparatus.

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 in 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 is 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 polymethyl styrene, 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. The carrier should be chosen in order that the charge to mass ratio of the blown-off toner is from about 10 to about 40 micro coulombs/gram and preferably from about 10 to 30 micro coulombs/gm.

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 examples in which parts and percentages are by weight unless otherwise specified.

EXAMPLE I

A copolymer of about 70 mol percent vinyl chloride and about 30 mol percent ethyl maleate having a second order glass transition temperature (Tg) of 57°C, a number average molecular weight of about 21,750 and a weight average molecular weight of about 51,350 by Gel Permeation Chromatography and marketed by Firestone Plastics under the grade designation FPC-471 is spray dried from a chloroform solution in a Bowen Laboratory Spray Dryer to obtain copolymer resin particles of from about 10 to 15 microns.

A small quantity of the resin particles are sprinkled onto a glass slide and placed in an oven preheated to 135°C for two minutes. Upon removal, visual observation readily indicates that the particles coalesce.

Six grams of the spray dried particles are subjected to the roll mill test previously described herein. After 500 hours, the particles are viewed under a scanning electron microscope. No particle failure can be observed. Substantially 100% of the particles are recovered after blow-off.

EXAMPLE II

A solution of the copolymer of Example I in chloroform having 5% carbon black dispersed therein is spray dried to form toner particles having a volume average particle size of about 13 microns and a number average particle size of about 4 to 5 microns and a resin content of about 95 percent and carbon black content of about 5 percent. About 0.25 percent of hydrophobic fumed silica sold as Aerosil R972 by DeGussa Incorporated is blended into the toner in a Lodige Blender.

An electrostatic developer is prepared by mixing 1 percent of the above mixture with a carrier material of 100 micron ferrite particles coated with 1.2 percent, based on the weight of the ferrite, of a polystyrene resin having a number average molecular

weight of about 160,000 and a weight average molecular weight of about 360,000. The polystyrene resin contains about 25% acetylene black. The coating is applied to the carrier core in a Wurster Spouting Fluidized Bed manufactured by Dairy Equipment Company, Madison, Wisconsin. The ferrite core is prepared in accordance with Example II of U.S. Patent 4,075,391.

This developer is used in an electrostatographic copier having a magnetic brush development system. After 250,000 copies, no change is visible in copy quality or in the character of the toner particles viewed under a scanning electron microscope. Further, throughout the test, the charge to mass ratio on the toner and the toner concentration after blow-off remain substantially constant, the former being about 30 microcoulombs per gram.

EXAMPLE III

A copolymer of 72 mol percent vinyl chloride and 28 mol percent dibutyl maleate is prepared by suspending about 100 parts of the monomers in the stated ratio and about 5 parts of lauroyl peroxide in about 500 parts by volume of a 1.25 percent polyvinyl alcohol-water solution which is agitated at 3000 r.p.m. for 30 seconds in a Waring Blender equipped with a Polytron mixing head to produce a droplet dispersion, the droplets having an average droplet size of about 12 microns. The reaction is continued at about 70°C with stirring at 80 r.p.m. for about six hours.

The polymer particles are separated by pouring the reaction mass into a large quantity of water and then centrifuging. The supernatatent liquid is decanted and the reaction product is washed three times with water.

The polymer thus formed is used in the procedure of Example II to prepare toner particles and developer.

This developer when used in an electrostatographic machine equipped with a magnetic brush development system gives excellent results over many copy cycles.

EXAMPLE IV

The procedure of Example III is repeated using diethyl maleate in place of dibutyl maleate. The resulting developer exhibits long life in a xerographic copier.

It is to be understood that the examples herein are by way of illustration and that other suitable copolymers as indicated above may be used throughout for those specifically employed.

CLAIMS:

1. An electrostatographic toner composition comprising a colorant and a resin, characterized in that the resin is a copolymer of vinyl chloride present in an amount of from 65 to 75 mole percent, and a lower alkyl maleate or fumarate, present in an amount of from 25 to 35 mole percent, which copolymer has an average number molecular weight of from 15,000 to 25,000 and a weight average molecular weight of from 45,000 to 55,000.

2. An electrostatographic toner composition in accordance with Claim 1 wherein the number average molecular weight of the copolymer resin is 22,000, and the weight average moleuclar weight of the copolymer resin is 51,000.

3. An electrostatograhpic toner composition in accordance with Claim 1 or Claim 2 wherein the lower alkyl maleate is ethyl maleate, propyl maleate, or butyl maleate.

4. An electrostatographic developer composition comprising the toner composition of any one of Claims 1 to 3 and carrier particles, the toner particles clinging to the surface of the carrier particles.

European Patent Office

EUROPEAN SEARCH REPORT

0022639
Application number
EP 80302229.2

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
D	US - A - 3 941 898 (SHIGERU SADAMATSU) + Column 6, lines 41-65 + ----	1

CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)

G 03 G 9/08
C 08 L 27/06

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	30-09-1980	SALTEN

EPO Form 1503.1 06.78