

[54] **TONER COMPOSITION EMPLOYING
POLYMER WITH SIDE-CHAIN
CRYSTALLINITY**

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96/1 SD

[56] **References Cited**

UNITED STATES PATENTS

3,558,492 1/1971 Proskow **252/62.1**

3,723,114 3/1973 Hagenbach **252/62.1**

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[57] **ABSTRACT**

Electrostatographic toner compositions are provided which melt over a narrow temperature range and which have the correct degree of hardness and toughness whereby they can be easily particulated, resist impaction, do not tend to deposit undesirable films on electrostatographic plates and do not fracture during use. The toner compositions of the present invention comprise a polymer selected from the group consisting of a crystalline homopolymer or copolymer having an amorphous backbone and side-chain crystallinity derived by the polymerization of a polymerizable mixture containing at least about 2 wt. % of a polymerizable monomer having a crystalline alkyl group of at least about 14 carbon atoms.

6 Claims, No Drawings

TONER COMPOSITION EMPLOYING POLYMER WITH SIDE-CHAIN CRYSTALLINITY

TONER COMPOSITIONS EMPLOYING POLYMER WITH SIDE-CHAIN CRYSTALLINITY

This invention relates in general to electrophotography and, more specifically, to an electrostatographic developer composition and to a method of using said developer composition.

It is known that images may be formed and developed on the surface of certain photoconductive materials by electrostatic means. The basic xerographic process, as taught by Carlson in U.S. Pat. No. 2,297,691 involves uniformly charging a photoconductive insulating layer and then exposing the layer to a light-and-shadow image which dissipates the charge on the portions of the layer which are exposed to light. The electrostatic latent image formed on the layer corresponds to the configuration of the light-and-shadow image. Alternatively, a latent electrostatic image may be formed on the plate directly by charging said plate in image configuration. This image is rendered visible by depositing on the image bearing layer a finely-divided electroscopic developing material called a "toner." A toner usually includes a thermoplastic resin and a colorant. A powdered developing material will normally be attracted to those portions of the layer which retain a charge, thereby forming a toner image corresponding to the latent electrostatic image. This powder image may then be transferred to paper or other receiving surfaces, and the transferred image may be made permanent by heating or other suitable fixing means. The above general process is also described in U.S. Pat. Nos. 2,357,809, 2,891,001 and 3,079,342.

The toner is an electroscopic material which is normally given a charge opposite to that of the electrostatic image which is to be developed. The toner comprises a resin and a colorant which may be a pigment, such as carbon black, or a dye. Several methods are known for imparting the desired charge to the toner particles and for applying the particles to the surface having the latent electrostatic image to be developed.

One development method, as described by Wise in U.S. Pat. No. 2,618,552, is known as "cascade" development. In this method, the development of the electrostatic latent image is accomplished by rolling or cascading a developer mixture comprising relatively large carrier particles, having fine toner particles electrostatically clinging to their surfaces, across the image-bearing surface. The composition of the carrier particles is so chosen as to triboelectrically charge the toner particles to the desired polarity. As the mixture cascades or rolls across the image-bearing surface, the toner particles are electrostatically deposited on and secured to the charged portions of the image, but not on the uncharged or background portions of the image. The carrier particles aid in removing any toner particles accidentally deposited on these background areas. This results in an excellent toner image with few toner particles in background areas.

Another system for developing electrostatic latent images which utilizes toner particles is known as "powder cloud" development. In this technique, a dispersion of electrically charged particles in a gaseous fluid is passed adjacent to the surface bearing the electrostatic latent image. Particles are drawn from the fluid disper-

sion to the charged areas on the image bearing plate to form a powder image on the plate. This technique is especially useful in continuous tone development. This form of development is further described in U.S. Pat. No. 2,221,776 to Carlson and in U.S. Pat. No. 2,935,234 to Heubner.

Still another method of developing electrostatic latent images is the so-called "magnetic brush" technique as disclosed, for example, by Giamo in U.S. Pat. No. 2,930,351. In this system, the toner is mixed with magnetic carrier particles to form a magnetic developer mix. The mix is carried by a magnetized member providing a magnetic field which holds the magnetic carrier particles in a brush-like configuration. When the brush is engaged with the electrostatic image-bearing surface, the toner particles are drawn from the brush by electrostatic forces and are deposited in image configuration on the surface.

Several other development methods are known which use toner particles to develop an electrostatic latent image. Among these are "touchdown" development as described by Gundlach in U.S. Pat. No. 3,166,432, "skid" development as described by Mayo in U.S. Pat. No. 2,895,847, "fur-brush" development as described by Greaves in U.S. Pat. No. 2,902,974 and "fluidized bed" development as described by Mott et al. in U.S. Pat. No. 3,008,826.

With each of the foregoing electrostatic image developing methods, the toner image may be fixed to the photoconductive surface or may be electrostatically transferred to a receiving sheet, such as by the method described by Carlson in U.S. Pat. No. 2,297,691.

Several different types of thermoplastic resins are presently used in toner particles. While generally capable of producing good quality images, these toner materials have serious deficiencies in certain areas. The toner resin must be capable of being conveniently fixed to the image supporting surface, e.g., by heat fusing or solvent vapor treatment. Where the toner is to be used onto a combustible surface such as paper, some materials have such a high fusing temperature that to get good adherence of the resin to the paper, it must be heated to a temperature such that the paper may scorch or even burn. On the other hand, some resins have such a low fusing temperature that they are tacky at ordinarily encountered ambient temperatures, thus resulting in an undesirable caking or agglomeration of particles during standing or storage. The temperature at which caking or agglomeration, i.e. blocking, occurs with a given resin is called the "blocking temperature" for that material. Conventional resinous toner materials are characterized by a blocking temperature substantially lower than the fusing temperature. Thus, a toner material having a blocking temperature substantially above the temperature normally encountered during storage also has a high fusing temperature thereby requiring an excessively large quantity of heat energy to fuse the toner material to the copy substrate, e.g., paper. When a high melting point toner is employed in a conventional xerographic copying or duplicating machine, either lower operating speeds or larger fusers are required in order to adequately fix the deposited toner image. The heat generated by high output fusers, endangers sensitive machine parts such as selenium photoconductive layers and also tends to elevate room temperature to the discomfort of the machine operator.

It is difficult and expensive to manufacture thermoplastic resins having consistently uniform molecular weights. Since amorphous thermoplastic resins consist of amorphous mixtures of polymer molecules of different molecular weights, they normally have wide, non-uniform melting ranges, they are difficult to reproduce and, consequently, fusing temperatures cannot be accurately predicted. The fusing devices must accordingly have larger than ordinarily necessary capacities to handle toner changes which may from time to time have unexpectedly high melting point ranges. Since the temperature in the fuser cannot be raised above the char point of the paper, often it is necessary to also reduce the speed with which the paper passes through the fuser unit of automatic xerographic copying and duplicating machines. Thus, it would be desirable to have a toner material with a balanced combination of blocking temperature and fusing temperature whereby the above-described difficulties would be avoided.

The polymeric component of toners for automatic electrostatic copying and duplicating machines should be both hard and tough. Soft toner compositions tend to form undesirable films on reusable electrostatic plates. These films, which have different electrical characteristics than the plate and are hygroscopic in nature, detrimentally affect the electrical conductivity of the plate when the machine is operated under conditions of high humidity. However, a polymeric material which is too tough is undesirable from the standpoint of its resistance to comminution such as by jet pulverization procedures. A polymer which is extremely hard and brittle is not advantageously used to form toner compositions since they tend to fracture when impinging upon each other or on relatively hard machine surfaces, forming a fine abrasive dust in the toner handling apparatus which may drift in air and cause premature deterioration of critical machine parts.

It has been attempted to prepare toners from crystalline polymers since such polymers are known to melt rather sharply rather than over a broad melting range; however, the generally available crystalline polymers are relatively conductive and adversely affect the stability of the latent image on the imaged electrostatic plate. Moreover, due to their high charge decay rate, such polymers are not capable of accepting and holding a charge of the correct polarity upon being mixed with and electrified by the surface of the carrier particles where used in cascade or magnetic brush developing systems.

Since most thermoplastic materials are deficient in one or more of the above areas, there is a continuing need for improvement in the materials used in the preparation of toner compositions.

It is therefore an object of this invention to provide developing materials which overcome the above noted deficiencies.

It is another object of this invention to provide toner compositions which are not tacky at ambient temperatures, but which fuse at relatively low temperatures.

It is still another object of this invention to provide toner compositions which do not tend to cake or agglomerate even after standing at room temperature for long periods of time.

It is another object of the present invention to provide toner compositions prepared from low melting polymeric materials which melt over a narrow tempera-

ture range and which have the correct degree of hardness and toughness whereby they can be easily particulated, resist impaction, do not tend to deposit undesirable films on electrostatic plates and do not fracture during use.

These and other objects are accomplished in accordance with the present invention by the provision of a new class of toner compositions prepared from polymers with side-chain crystallinity, having a polymer melting point above about 40°C., a weight average molecular weight of more than 2000, said polymers having alkyl side chains of at least 14 carbon atoms. Such polymers, which can be prepared by addition or condensation polymerization of monomers, containing a long chain alkyl radical, with or without other appropriate copolymerizable monomers, when mixed with a colorant and, optionally up to about 90 wt. percent of another thermoplastic polymer material provide highly useful, low melting, free flowing toners which melt within a range, measured visually, of less than about 10°C. Toner compositions of this invention have many advantageous properties which can be attributed to the crystalline nature of the polymer and yet, surprisingly, are not encumbered with the disadvantages normally associated with toners based upon crystalline polymeric components. Thus, these polymers are sharp melting and exhibit rapid changes in melt of viscosity with temperature, a desirable property which results from the crystalline structure of the polymer. However, although the polymers are crystalline, they do not have a high charge decay rate and are not highly conductive, and thus, they are capable of producing developed latent images of high quality and optical image density. The side chain crystalline polymers advantageously have a melting point within the range of about 40°C. to 135°C., and preferably between 60°-100°C., a range which is considerably lower than the polymers conventionally used in the preparation of toner compositions.

Suitable polymers for use in the invention have a non-crystalline (i.e., amorphous) backbone with pendant crystalline alkyl groups. The chemical structure of the backbone is not of critical importance since it merely serves to join together the crystalline side-chains which actually provide the desirable melting characteristics to the polymers. Thus, the polymer may be an addition or condensation polymer prepared by any process so long as such process is capable of giving a product having an amorphous backbone with side-chain crystallinity.

Any suitable particulate resin having an amorphous backbone and side-chain crystallinity imparted by a C₁₄ or longer alkyl group, a sharp melting point in the range of 40°-135°C., a molecular weight of at least 2000 and a volume resistivity of at least about 10¹² ohm-cms, may be used herein. Typical polymers meeting the above requirements have the characteristic <C=C> monomeric structure made, for example, from the following vinyl monomers: esters of C₁₄ or longer saturated alcohols with mono and dibasic unsaturated acids such as long chain alkyl acrylates, methacrylates and haloacrylates, di-(C₁₄ or longer alkyl) fumarates and maleates, and mixtures thereof; vinyl ketones such as C₁₄ or longer alkyl vinyl ketones, e.g., docosyl vinyl ketone; vinyl esters such as vinyl docosylate; unsaturated aromatic compounds such as p-(C₁₄ or longer alkyl) styrene and alpha-methyl styrene, 1-vinyl-4 (C₁₄ or longer alkyl) naphthalene, and mixtures thereof; copolymers of

the foregoing monomers with up to 20% other polymerizable vinyl compounds such as acrylamide, methacrylamide, acrylonitrile, methacrylonitrile, haloacrylonitrile, and phenylacrylonitrile, N-substituted unsaturated amides such as N,N-di-(C₁₄ or longer alkyl) acrylamide, N-(C₁₄ or longer alkyl) acrylamide and mixtures thereof; unsaturated ethers such as vinyl alkyl ethers of C₁₄ or longer alcohols or thioalcohols and mixtures thereof; unsaturated heterocyclic compounds such as C₁₄ or longer alkyl substituted vinyl pyridine, vinyl furan, vinylcoumarone, N-vinyl carbazole, and mixtures thereof; as well as condensation polymers including polyesters, such as linear, unsaturated and alkyd types made, for example, by reacting a difunctional acid or anhydride such as phthalic, isophthalic, terephthalic, malic, maleic, citric, succinic, glutaric, adipic, tartaric, pimelic, suberic, azelaic, sebacic and camphoric with a branched diol such as docosane-1,2-diol; polyethers such as the epoxy type made, for example, by condensing epichlorohydrin with a C₁₄ or longer alkyl branched glycol e.g., docosyl-1,2-diol; other polyethers made, for example, by reacting formaldehyde with a C₁₄ or longer alkyl-1,2-glycol; polyurethanes prepared, for example, by reacting a diisocyanate such as toluene-2,4-diisocyanate methylene bis (4-phenylisocyanate), bitolylene diisocyanate, 1,5-naphthalene diisocyanate, and hexamethylene diisocyanate with a branched glycol of 14 or more carbons, phenol aldehyde resins made, for example, by condensing a C₁₄ or longer alkyl substituted resorcinol, phenol or cresol with formaldehyde, furfural or hexamethylene tetramine; C₁₄ or longer-(alkyl, or alkaryl) silicones; etc.

Any suitable mixture of a block or graft copolymer or terpolymer of the above materials may be used in the process of this invention.

The toner should be of a particle size which is suitable for the particular development process in which it is to be employed, as each development system has its own optimum particle size requirements. Particle sizes in the range of 5-30 μ , are generally useful.

The toner may be used to develop electrostatic latent images as described above, e.g., cascade and magnetic brush developing techniques. When thus used, it is admixed with carrier particles (the average size of which ranges between 50 μ and 1000 μ) selected so as to impart a charge of the desired polarity to the toner particles whereby the latter are caused to electrostatically adhere to, and coat each carrier particle. The carrier particles may be either electrically conductive or insulating and magnetic or non-magnetic. Developer compositions generally contain 0.5-10 wt. % toner and 90-99.5 wt. % carrier. When a positive reproduction of the electrostatic latent image is desired, the carrier particle is selected so that the toner particles acquire a charge having the opposite polarity to that of the electrostatic latent image. Alternatively, if a reversal reproduction of the electrostatic latent image is desired, the carrier is selected so that the toner particles acquire a charge having the same polarity as that of the electrostatic latent image. Typical of the carriers which may be employed are those, for example, described by Walkup in U.S. Pat. No. 2,618,551 and by Wise in U.S. Pat. No. 2,618,552.

The toner compositions of the present invention may be employed to develop latent electrostatic images on the surface of any suitable latent electrostatic image-

bearing surface, photoconductive or otherwise. Typical of the photoconductors which may be employed are those, for example, described by Bixby in U.S. Pat. No. 2,970,906 and by Middleton et al. in U.S. Pat. No. 3,121,006.

Polymers with side-chain crystallinity form excellent toners primarily because of their durability and excellent melting characteristics. Such polymers have a melting temperature which is substantially the same as their blocking temperature. Thus, a crystalline polymer may be selected for toner use which has a blocking temperature sufficiently above ambient temperatures to preventing blocking during storage or use. On the other hand, the melting temperature will be approximately the same as the blocking temperature and, therefore, much lower than the melting temperature of the usual amorphous toner polymers. The sharp melting temperature of crystalline polymers permits rapid fusing of toner images at a relatively low temperature thereby conserving heat energy and protecting sensitive machine parts from the deleterious effects of excessive heating.

The toner material may be colored by any conventional technique, e.g., dispersing a dye or pigment in the monomer before polymerization, by incorporating the colorant in the polymer melt before formation of the particles, by incorporating the color in a solution of the polymer before particle formation, by surface dyeing the toner particles or by any desirable combination of these techniques.

Any suitable pigment or dye may be employed as the colorant for the toner particles. Typical colorants include carbon black, e.g., furnace black or channel black, like Black Pearls L or Neospectra Mark II, and mixtures thereof. Carbon black is the preferred colorant since it is easily dispersed in the crystalline polymer and has an intense black color.

Any suitable method for forming small particles of the desired size from the polymeric toner may be used as desired. Typically, small particles may be formed by grinding, emulsion spray drying, solution spray drying, etc. Grinding of polymeric crystalline materials may tend to destroy crystallinity and induce reactions. To prevent such reactions from occurring, it may be preferred to cool the polymer mass with dry ice and grind them in the cooled state.

The methods by which the useful polymer can be prepared are well known to those skilled in the art. Reference is made to the following texts dealing with polymerization techniques which can be employed:

1. W. R. Sorenson and T. W. Campbell, "Preparative Methods of Polymer Chemistry", Second Edition, Interscience 1968; and,
2. G. E. Ham, "Vinyl Polymerization", Marcel Dekker 1967.

The long side-chain acrylates (and methacrylates) and copolymers thereof with styrene are particularly preferred. They can be prepared by vinyl polymerization of long chain alkyl acrylates (or methacrylates).

The preferred method for preparing the long side-chain acrylate or methacrylate monomer is transesterification of ethyl acrylate or methacrylate with a long chain monofunctional alcohol. Typically, 2.5 moles of ethyl acrylate are allowed to react with 1.0 mole n-docosanol in the presence of 0.01 mole percent phenothiazine and 1.0 mole percent tetra-alkyl titanate between 80°-120°C. The products of the reaction are

equimolar quantities of docosyl acrylate and ethyl alcohol accompanied by unchanged ethyl acrylate. The transesterification reaction is driven to completion by removal of the ethanol/ethyl acrylate azeotrope which may be monitored by refractive index or gas liquid chromatography. Product formation may also be monitored by gas liquid chromatography of docosanol/docosyl acrylate ratio, which indicates approximately 95% conversion in 2 hours. The last traces of ethyl acrylate are removed under vacuum. The resultant product is generally sufficiently pure for polymerization purposes. It may then be allowed to form homopolymer, or be polymerized with styrene to form block or mixtures of block copolymers and homopolymers by any suitable method; for example by bulk, solution, suspension or emulsion polymerization techniques.

In a typical solution polymerization 0.33 moles of docosyl acrylate, 0.33 moles of styrene and 1.0 mole of benzene are heated to 80°C. for 10 hours in the presence of 1.61 g. of azoisobutyronitrile, a free radical catalyst. The resultant product is poured into a dish and heated overnight in a vacuum oven at 75°C. to yield a pale yellow solid, m.p. 59.5°-61.0°C. Gel permeation chromatography shows no significant amount of residual monomers.

Typically, developer materials can be prepared from carriers and toners where the latter may constitute from 0.2-5.0 percent by weight of the sample. The optimum ratio of carrier to toner in a developer depends upon the development system utilized. Further, for optimum performance in any specific development and cleaning mode various types of additives may be required. Each development system has its own specific type of additive requirement for optimum performance. Thus in cascade development a hydrophobic metal salt of a higher fatty acid is often added to the toner for improved cleaning (U.S. Pat. No. 3,577,345).

The side-chain crystalline polymers used in the toners of the present invention may be used in conjunction with other non-crystalline polymers to form blends therewith. The non-crystalline polymers, when used alone, generally form high and broad melting toner composition. However when used in conjunction with the polymers having side-chain crystallinity the resultant toner compositions have a distinct fusing advantage over toners prepared only from amorphous polymer materials. Thus, blends of amorphous polymers which side-chain crystalline polymers are useful as the presence of even very low concentrations of the latter has a significant viscosity lowering effect. The degree of viscosity lowering is dependent on the nature of the side-chain crystalline polymer and the amount of it blended with the amorphous polymer. Compositions of blends containing as little as 1% side-chain crystalline polymer will have a fusing advantage over the amorphous polymer used by itself. Blends containing 10-40 wt.% lead to toner compositions with yet greater fusing advantage. Toner compositions with even higher percentages of side-chain crystalline polymer e.g. 90 wt. % of higher can also be employed.

Any conventional blending procedure may be used to form the crystalline-amorphous polymer blend described above. the polymer materials and the pigment may be blended simultaneously, or, if desired, the pigment may be blended with one polymer and the resultant mixture then blended with the other polymer. Inti-

mate mixing can be achieved by any milling or plasticating device. Because the polymer with side-chain crystallinity melts considerably below the amorphous polymer, it may be desirable to blend the pigment with the crystalline polymer and then blend the resultant paste-like material with the viscous amorphous polymer. This method avoids the difficulty which results when a very viscous liquid is mixed with another liquid of low viscosity.

Among the amorphous materials which can be admixed with the polymers having side-chain crystallinity described above are: acrylics, polystyrene, polystyrene/vinyl esters (e.g. styrene/n-butyl methacrylate), polyethylene, ethylene-vinyl acetate polymers, ABS, polyethers, polyesters and vinyl polymers.

A particularly useful blend results when a vinyl polymer having side-chain crystallinity, such as a poly(alkyl acrylate-styrene copolymer), is admixed with another polyacrylate, such as a copolymer of styrene with a lower acrylate.

The following examples further define and describe exemplary methods of preparing the toners and developers of the present invention and of utilizing them for developing electrostatic latent images. Parts and percentages are by weight unless otherwise indicated.

EXAMPLE I

Toners are prepared by melting a thermoplastic resin, blending in about 10 percent by weight based on the weight of resin of finely divided carbon black, cooling to form a solid mass and sub-dividing the mass in a micropulverizer to yield particles having an average size of about 10 to about 15 microns. The thermoplastic materials used are as follows:

- a. a conventional toner based on an amorphous styrene/n-butyl methacrylate polymer;
- b. an amorphous styrene/n-butyl methacrylate polymer and a plasticizer, which is a mixture of ortho and para toluene sulfonamide, commercially available from Monsanto under the trademark Santicizer 9;
- c. a docosyl acrylate polymer having a melting point of 62°-63°C;
- d. a copolymer prepared from about 70 mol percent docosyl acrylate and about 30 mol percent styrene having a melting point of 61°-63°C.;
- e. a tetracosyl methacrylate polymer having a melting point of 64°-66°C;
- f. poly [2,2'-(p-phenylene dioxy) ethylene azelate] having a softening point of 70°-105°C.

About 2 parts of each of the toner samples to be tested are mixed with about 200 parts carrier beads. The carrier beads are prepared as described in U.S. Pat. No. 2,618,551. Each mixture is cascaded across a photoconductive surface bearing an electrostatic latent image. The toner is deposited on the surface in image configuration. Each formed image is then transferred to a paper receiving sheet by the process described in U.S. Pat. No. 2,576,047.

The individual sheets prepared with each toner are then heated to temperatures of 60°, 80°, 100°, 120° and 140°C. in an air circulating oven. The quality of affixation obtained with each toner at each temperature, and the resistance of fixed images to abrasion are then tested by fastening each sheet to a full page abrading cylinder having a diameter of about 10 inches. A conventional Xerox 813 cleaning web is pressed against the copy sheet by a spring loaded roller under a spring

tension of about 40 pounds per linear inch. By rotating the cylinder bearing the copy sheet, the entire toner image on the copy sheet is abraded by frictional contact with the web. A minimum fusing temperature is established when all the test characters are legible after an abrasion run of 5 revolutions of the abrading cylinder. The results of this test are given in Table I.

TABLE I

DURABILITY OF HEAT FIXED DEVELOPED IMAGE					
Thermoplastic Material	60°C.	80°C.	100°C.	120°C.	140°C.
(a)	none	none	none	poor	good
(b)	none	none	poor	poor	poor
(c)	poor	good	good	good	good
(d)	poor	good	good	good	good
(e)	poor	good	good	good	good
(f)	none	poor	poor	good	good

As can be seen the above Table, a temperature of about 140°C. is required to obtain good fixation with conventional toner (a). Toners using thermoplastic material (f) require temperatures of approximately 120°C. Toners using thermoplastic material (b) do not achieve good fixation at even 120°C. for good fixation. Good fixation is obtained only with toners (c), (d) and (e) at a temperature of about 80°C. The toner using thermoplastic material (b) is susceptible to abrasion damage even beyond its fusion fixing temperature.

A sample prepared as described above using a fixation temperature sufficient to allow fixation of the thermoplastic materials is folded and creased sharply across image areas. Upon unfolding, no cracking or crumbling of the image is observed with material (a) and (c)-(f). However, severe flaking and cracking of the image areas is observed at the creases with toner material (b).

EXAMPLE II

About 9 parts of poly (docosyl acrylate) melting point 62°-63°C. are heated to about 80°C. The resultant molten resin is blended with about one part of finely divided carbon black and the pigmented resin in molten state is emulsified in water at a temperature of about 80°C. The emulsion is cooled below the melting point of the resin and filtered. The black colored particles having an average diameter of about 8 microns are then dried by a heated air-stream and about 2 parts of the resultant toner are then mixed with about 200 parts of carrier beads prepared by the method disclosed in U.S. Pat. No. 2,618,551 (Walkup). This mixture is cascaded across a selenium surface bearing an electrostatic latent image. The toner deposits on the surface bearing an electrostatic latent image. The toner deposits on the surface in image configuration and the image is electrostatically transferred to a paper receiving sheet. The sheet is placed in a heated oven at a temperature of about 70° to 75°C. for about 10 seconds giving a permanently fixed image conforming to the original, and having good density and clean background areas.

EXAMPLE III

A crystalline thermoplastic resin is prepared by copolymerizing 70 mole % of docosyl acrylate and about 30 mole % of styrene. This resin is heated to about 80°C. and into the resultant molten material is blended

about 1 part of finely divided carbon black. The pigmented material is poured onto a flat surface where it is allowed to cool to room temperature. The cooled material is micropulverized to yield particles of an average size of about 10 microns. The resultant toner particles are mixed with magnetic carrier material and brought into contact with the surface bearing an electrostatic latent image as described in U.S. Pat. No. 2,930,351. The particles are attracted to the surface in image configuration and the resultant developed image is transferred to a paper receiving sheet which is then heated to about 65°C. for about 10 seconds to fuse the resin. Upon cooling to room temperature, a permanently fixed, dense image conforming to the original copy is obtained.

EXAMPLE IV

A crystalline thermoplastic resin is prepared by copolymerizing about 70 mole % of tetracosyl acrylate and about 30 mole % of styrene. The resin is melted by heating to about 80°C. and blended with about 1 part of finely divided carbon black. The molten material is poured onto a flat surface and allowed to cool to room temperature. The cooled mass is finely subdivided in a micropulverizer to yield particles having an average size of about 10 microns. The resultant toner particles are mixed with a magnetic carrier material and brought into contact with a surface bearing an electrostatic latent image as described above. The toner particles are attracted to the surface in image configuration and then transferred to a paper receiving sheet which is then heated to about 65°C. for about 10 seconds to fuse the resin. Upon cooling to room temperature the image is found to be permanently fixed to the paper sheet and is a high quality reproduction of the original.

EXAMPLE V

A crystalline thermoplastic resin is prepared by copolymerizing about 70 mole % of di-(n-docosyl) fumarate and about 30 mole % of styrene. The resin is melted by heating to about 100°C. and blended with about 1 part of finely divided carbon black. The molten material is poured onto a flat surface and allowed to cool to room temperature. The cooled mass is finely subdivided in a micropulverizer to yield particles having an average size of about 10 microns. The resultant toner particles are mixed with a magnetic carrier material and brought into contact with a surface bearing an electrostatic latent image as described above. The toner particles are attracted to the surface in image configuration and then transferred to a paper receiving sheet which is then heated to about 65°C. for about 10 seconds to fuse the resin. Upon cooling to room temperature the image is found to be permanently fixed to the paper sheet and is a high quality reproduction of the original.

EXAMPLE VI

About 9 parts of poly (docosyl vinyl ketone) are heated to about 80°C. and the resultant molten resin is blended with about 1 part of finely divided carbon black and the pigmented resin in molten state is emulsified in boiling water. The emulsion is cooled below the melting point of the resin and filtered. The black colored particles having an average diameter of about 8 microns are then dried by heated air. About 2 parts of the resultant toner are then mixed with about 200 parts

of carrier beads prepared by the method disclosed in U.S. Pat. No. 2,618,551 (Walkup). This mixture is cascaded across a selenium surface bearing an electrostatic latent image. The toner deposits on the surface in image configuration and the image is electrostatically transferred to a paper receiving sheet. The sheet is placed in a heated oven for about 10 seconds giving a permanently fixed image conforming to the original, and having good density and clean background areas.

EXAMPLE VII

A crystalline thermoplastic resin is prepared by copolymerizing 70 mole % of vinyl docosylate and about 30 mole % of styrene. This resin is heated to about 80°C. and into the resultant molten material is blended about 1 part of finely divided carbon black. The pigmented material is poured onto a flat surface where it is allowed to cool to room temperature. The cooled material is micropulverized to yield particles of an average size of about 10 microns. The resultant toner particles are mixed with magnetic carrier material and brought into contact with the surface bearing an electrostatic latent image as described in U.S. Pat. No. 2,930,351. The particles are attracted to the surface in image configuration and the resultant developed image is transferred to a paper receiving sheet which is then heated to about 65°C. for about 10 seconds to fuse the resin. Upon cooling to room temperature, a permanently fixed, dense image conforming to the original copy is obtained.

EXAMPLE VIII

A crystalline thermoplastic resin is prepared by copolymerizing 70 mole % of p-(docosyl) styrene and about 30 mole % of styrene. This resin is heated to about 100°C. and into the resultant molten material is blended about one part of finely divided carbon black. The pigmented material is poured onto a flat surface where it is allowed to cool to room temperature. The cooled material is micropulverized to yield particles of an average size of about 10 microns. The resultant toner particles are mixed with magnetic carrier material and brought into contact with the surface bearing an electrostatic latent image as described in U.S. Pat. No. 2,930,351. The particles are attracted to the surface in image configuration and the resultant developed image is transferred to a paper receiving sheet which is then heated for about 10 seconds to fuse the resin. Upon cooling to room temperature, a permanently fixed, dense image conforming to the original copy is obtained.

EXAMPLE IX

A crystalline thermoplastic resin is prepared by copolymerizing 70 mole % of N,N-di-(tetracosyl) acrylamide and about 30 mole % of styrene. This resin is heated to about 100°C. and into the resultant molten material is blended about 1 part of finely divided carbon black. The pigmented material is poured onto a flat surface where it is allowed to cool to room temperature. The cooled material is micropulverized to yield particles of an average size of about 10 microns. The resultant toner particles are mixed with magnetic carrier material and brought into contact with the surface bearing an electrostatic latent image as described in U.S. Pat. No. 2,930,351. The particles are attracted to

the surface in image configuration and the resultant developed image is transferred to a paper receiving sheet which is then heated to about 75°C. for about 10 seconds to fuse the resin. Upon cooling to room temperature, a permanently fixed, dense image conforming to the original copy is obtained.

EXAMPLE X

A crystalline thermoplastic resin is prepared by copolymerizing 70 mole % of vinyl docosyl ether and about 30 mole % of styrene. This resin is heated to about 80°C. and into the resultant molten material is blended about 1 part of finely divided carbon black. The pigmented material is poured onto a flat surface where it is allowed to cool to room temperature. The cooled material is micropulverized to yield particles of an average size of about 10 microns. The resultant toner particles are mixed with magnetic carrier material and brought into contact with the surface bearing an electrostatic latent image as described in U.S. Pat. No. 2,930,351. The particles are attracted to the surface in image configuration and the resultant developed image is transferred to a paper receiving sheet which is then heated to about 65°C. for about 10 seconds to fuse the resin. Upon cooling to room temperature, a permanently fixed, dense image conforming to the original copy is obtained.

EXAMPLE XI

A crystalline thermoplastic resin is prepared by copolymerizing 70 mole % of 2 vinyl-4 docosyl pyridine and about 30 mole % of styrene. This resin is heated to about 100°C. and into the resultant molten material is blended about one part of finely divided carbon black. The pigmented material is poured onto a flat surface where it is allowed to cool to room temperature. The cooled material is micropulverized to yield particles of an average size of about 10 microns. The resultant toner particles are mixed with magnetic carrier material and brought into contact with the surface bearing an electrostatic latent image as described in U.S. Pat. No. 2,930,351. The particles are attracted to the surface in image configuration and the resultant developed image is transferred to a paper receiving sheet which is then heated to about 75°C. for about 10 seconds to fuse the resin. Upon cooling to room temperature, a permanently fixed, dense image conforming to the original copy is obtained.

EXAMPLE XII

A mixture consisting of 70g. styrene/n-butylmethacrylate (65/35) amorphous copolymer and 20 g. of docosyl acrylate/styrene (90/10) side chain crystalline copolymer is heated to about 120°C. and 10 g. of Black Pearls carbon black is blended into the resultant molten material. The pigmented material is poured onto a flat surface where it is allowed to cool to room temperature. The cooled material is micropulverized to yield particles of an average size of about 10 microns. The resultant toner particles are mixed with magnetic carrier material and brought into contact with the surface bearing an electrostatic latent image as described in U.S. Pat. No. 2,930,351. The particles are attracted to the surface in image configuration and the resultant developed image is transferred to a paper receiving sheet. The receiving sheet is heated to about 120°C. for about 10 seconds to fuse the resin.

EXAMPLE XIII

A toner and carrier mixture, similar to that described in Example XII except that the crystalline toner is omitted, is employed to make copies by the procedure described in Example XII. A fusing temperature of 160°-170°C. is required to permanently affix the image to the copy substrate.

EXAMPLE XIV

A control toner mixture is prepared by blending 90 parts of a crystalline polyethylene of over 100,000 molecular weight with 10 parts of carbon black. The resultant thoroughly blended mixture is cooled with liquid nitrogen and then finely subdivided to yield toner particles having an average particle size of about 10 microns. Cooling below room temperature is necessary to avoid deposition of a film of the resin on the surface of the pulverizer. About one part of the toner is mixed with about 100 parts of Xerox 813 carrier. The resultant developer is used to make 8,000 copies in a Xerox 813 copying machine. The copies, particularly near the termination of the test, are characterized by very low density image and high background development. An examination of the xerographic drum after the termination of the test reveals a heavy film of toner over the surface of the drum.

Other materials than those specifically enumerated above may be substituted for those used in the examples with similar results. For example, other ingredients may be added to the development compositions or the toner compositions to enhance or otherwise modify

their properties.

Other modifications and ramifications of the present invention will occur to those skilled in the art upon a reading of the foregoing specification. These are intended to be included within the scope of the invention which is only limited by the appended claims.

What is claimed is:

1. An electrostatographic developer composition comprising about 0.5 to 10 wt. percent of toner particles, said toner particles comprising a polymer selected from the group consisting of a crystalline homopolymer or copolymer having an amorphous backbone and side-chain crystallinity derived by the polymerization of a polymerizable mixture containing at least about 2 wt. percent of a polymerizable monomer having a crystalline alkyl group of at least about 14 carbon atoms and about 90 to 99.5 wt. percent of carrier particles.
2. The composition of claim 1 wherein the toner comprises a crystalline homopolymer.
3. The composition of claim 2 wherein the backbone of the homopolymer is derived by the polymerization of a vinyl monomer.
4. A process for developing an electrostatic latent image comprising contacting a latent image bearing member with the developer composition of claim 1 whereby toner is attracted to said member in imagewise configuration.
5. The process of claim 4 wherein said toner comprises a crystalline homopolymer.
6. The process of claim 5 wherein said toner is derived by the polymerization of a vinyl monomer.

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