SOLID DEVELOPER FOR LATENT ELECTROSTATIC IMAGES

3,590,000

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ABSTRACT OF THE DISCLOSURE

A finely-divided, rapid melting toner comprising a colorant, a solid, stable hydrophobic metal salt of a fatty acid, and a polymeric esterification product of a dicarboxylic acid and a diol comprising a diphenol.

BACKGROUND OF THE INVENTION

This invention relates to imaging systems, and more particularly, to improved xerographic developing materials, their manufacture and use.

The formation and development of images on the surface of photoconductive materials by electrostatic means is well known. The basic xerographic process, as taught by C. F. Carlson in U.S. Pat. 2,297,691, involves placing a uniform electrostatic charge on a photoconductive insulating layer, exposing the layer to a light-and-shadow image to dissipate the charge on the areas of the layer exposed to the light and developing the resulting latent electrostatic image by depositing on the image a finely-divided electroscopic material referred to in the art as "toner." The toner will normally be attracted to those areas 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 a support surface such as paper. The transferred image may subsequently be permanently affixed to the support surface by heat. Instead of latent image formation by uniformly charging the photoconductive layer and then exposing the layer to a light-and-shadow image, one may form the latent image by directly charging the layer in image configuration. The powder image may be fixed to the photoconductive layer by elimination of the powder image transfer step is desired. Other suitable fixing means such as solvent or overcoating treatment may be substituted for the foregoing heat fixing steps.

Several methods are known for applying the electroscopic particles to the latent electrostatic image to be developed. One development technique, as disclosed by E. N. Wise in U.S. Pat. 2,618,552, is known as "cascade" development. In this method, a developer material comprising relatively large carrier particles having finely-divided toner particles electrostatically coated thereon is conveyed to and rolled or cascaded across the electrostatic latent image-bearing surface. The composition of the carrier particles is so selected 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 and secured to the charged portion of the latent image and are not deposited on the charged or background portions of the image. Most of the toner particles accidentally deposited in the background are removed by the rolling carrier, due apparently, to a greater electrostatic attraction between the toner and the carrier than between the toner and the discharged background. The carrier and excess toner are then recycled. This technique is extremely good for the development of line copy images.

Another method of developing electrostatic images is the "magnetic brush" process as disclosed, for example, in U.S. Pat. 2,874,063. In this method, a developer material containing toner and magnetic carrier particles are carried by a magnet. The magnetic field of the magnet causes alignment of the magnetic carrier into a brush-like configuration. This "magnetic brush" is engaged with the electrostatic image-bearing surface and the toner particles are drawn from the brush to the latent image by electrostatic attraction.

Still another technique for developing electrostatic latent images is the "powder cloud" process as disclosed, for example, by C. F. Carlson in U.S. Pat. 2,221,776. In this method, a developer material comprising electrically charged toner particles in a gaseous fluid is passed adjacent to the surface bearing the latent electrostatic image. The toner particles are drawn by electrostatic attraction from the gas to the latent image. This process is particularly useful in continuous tone development.

Other development methods such as "touchdown" development as disclosed by R. W. Gundlach in U.S. Pat. 3,166,432 may be used where suitable.

Although some of the foregoing development techniques are employed commercially today, the most widely used commercial xerographic development technique is the process known as "cascade" development. A general purpose office copying machine incorporating this development method is described in U.S. Pat. 3,099,943. The cascade development technique is generally carried out in a commercial apparatus by cascading a developer mixture over the upper surface of an electrostatic latent image-bearing drum having a horizontal axis. The developer is transported from a trough or sump to the upper portion of the drum by means of an endless belt conveyor. After the developer is cascaded downward along the upper quadrant surface of the drum into the sump, it is recycled through the developing system to develop additional electrostatic latent images. Small quantities of toner are periodically added to the developing mixture to compensate for the toner depleted by development. The resulting toner image is usually transferred to a receiving sheet and thereafter fused by suitable means such as an oven. The surface of the drum is thereafter cleaned for reuse. This imaging process is then repeated for each copy produced by the machine and is ordinarily repeated many thousands of times during the usable life of the developer.

Thus, it is apparent from the description presented above as well as in other development techniques, that the toner is subjected to severe mechanical attrition which tends to break down the particles into undesirable dust fines. The formation of fines is retarded when the toner contains a tough, high molecular weight resin which is capable of withstanding the shearing and impact forces imparted to the toner in the machine. Unfortunately, many high molecular weight materials cannot be employed in high speed automatic machines because they cannot be rapidly fused during a powder image heat fixing step. Attempts to rapidly fuse a high melting point toner by means of oversized high capacity heating units have been confronted with the problems of preventing the charring of paper receiving sheets and of adequately dissipating the heat evolved from the fusing unit or units. In some cases, the receiving sheet has actually combusted and flames after passage through the fusing unit. Thus, in order to avoid charring or combustion, additional equipment such as complex and expensive cooling units are necessary to properly dispose of the large quantity of heat generated by the fuser. Incomplete removal of the heat evolved will result in operator discomfort and damage to heat sensitive machine components. Further, the increased space occupied by and the high operating costs of the heating and cooling units often outweigh the advantages achieved by the increased machine speed. On the
other hand, low molecular weight resins which are easily heat fused at relatively low temperatures are usually undesirable because these materials tend to form thick films on reusable photoconductor surfaces. These films tend to cause image degradation and contribute to machine maintenance down time. Many low molecular weight resins decompose when subjected to fusing conditions in high speed copying and duplicating machines. In addition, low molecular weight resins tend to form tacky images on the copy sheet which are easily smudged and often offset to other adjacent sheets. Additionally, low molecular weight resins are often extremely difficult or even impossible to comminute in conventional grinding apparatus. Also, the toner material must be capable of accepting a charge of the correct polarity when brought into rubbing contact with the surface of carrier materials in cascade or touchdown development systems. The triboelecric and flow characteristics of many toners are adversely affected by changes in the ambient humidity. For example, the triboelectric values of some toners fluctuate with changes in relative humidity and are not desirable for employment in xerographic systems, particularly in precision automatic machines which require toners having stable and predictable triboelectric values. Another factor affecting the stability of carrier triboelectric properties is the tendency of some toner materials to “impact” on the surface of carrier particles. When developers are employed in automatic cascade developing machines and recycled through many cycles, the many collisions which occur between the carrier and toner particles in the machine cause the toner particles carried on the surface of the carrier particles to be welded or otherwise forced into the surface as carrier particles. The gradual accumulation of permanently attached toner material on the surface of carrier particles causes a change in the triboelectric value of the carrier particles and directly contributes to the degradation of copy quality by eventual destruction of the toner carrying capacity of the carrier. Numerous known carriers and toners are abrasive in nature. Abrasive contact between toner particles, carriers, and xerographic imaging surfaces accelerates mutual deterioration of these components. Replacement of carriers and electrostatic image bearing surfaces is expensive and time consuming. Xerographic copies should possess good line image contrast as well as acceptable solid area coverage. However, when a process is designed to improve either line image contrast or solid area coverage, reduced quality of the other can be expected. Attempts to increase image density by depositing greater quantities of toner particles on the latent electrostatic image are usually rewarded with an undesirable increase in background deposits. Since most thermoplastic materials are deficient in one or more of the above areas, there is a continuing need for improved toners and developers.

SUMMARY OF THE INVENTION

It is, therefore, an object of this invention to provide a developer overcoming the above noted deficiencies. It is another object of this invention to provide a toner which is stable at toner fusing conditions in high speed copying and duplicating machines. It is another object of this invention to provide a toner which is triboelectrically stable under varying humidity conditions. It is another object of this invention to provide a toner which is resistant to smearing. It is another object of this invention to provide a toner which is resistant to agglomeration. It is another object of this invention to provide a toner which is readily removable by carriers from background areas during image development. It is another object of this invention to provide a toner which may be easily cleaned from electrostatic imaging surfaces. It is another object of this invention to provide a toner which reduces mechanical abrasion of electrostatic imaging surfaces. It is another object of this invention to provide a toner which is effective at low initial electrostatic surface potentials. It is another object of this invention to provide a toner which forms dense toner images. It is another object of this invention to provide a toner which is readily transferable from a xerographic imaging surface to a transfer surface. It is another object of this invention to provide a toner which is resistant to mechanical attrition during the development process. It is another object of this invention to provide a toner and developer having physical and chemical properties superior to those of known toners and developers. The objectives and others are accomplished by providing a xerographic toner comprising a colorant, a solid, stable hydrophobic metal salt of a fatty acid, and a polymeric esterification product of a dicarboxylic acid and a diol comprising a diphenol. The diphenol reactant has the general structure:

\[
\text{H(OH)}_2\text{R}^\text{O}-\text{O}^\text{-}\text{R}^\text{R}\text{O}-\text{O}\text{H}
\]

wherein R represents substituted and unsubstituted alkylene radicals having from 2 to 12 carbon atoms, alkyldiene radicals having from 1 to 12 carbon atoms, and cycloalkyldiene radicals having from 3 to 12 carbon atoms; \( R' \) and \( R'' \) represent substituted and unsubstituted alkylene radicals having from 2 to 12 carbon atoms, alkylene arylene radicals having from 8 to 12 carbon atoms and arylene radicals; \( X \) and \( X' \) represents hydrogen or an alkyl radical having from 1 to 4 carbon atoms; and \( n_1 \) and \( n_2 \) each is at least 1 and the average sum of \( n_1 \) and \( n_2 \) is less than 21. Diphenols wherein \( R \) represents an alkyldiene radical having from 2 to 4 carbon atoms and \( R' \) and \( R'' \) represents an alkylene radical having from 3 to 4 carbon atoms are preferred because greater blocking resistance, increased definition of xerographic characters, and more complete transfer of toner images are achieved. Optimum results are obtained with diols in which \( R \) is a isopropylidene radical and \( R' \) and \( R'' \) are selected from the group consisting of propylene and butylene radicals because the resins formed from these diols possess higher agglomeration resistance and penetrate extremely rapidly into paper receiving sheets under fusing conditions. Dicarboxylic acids having from 3 to 5 carbon atoms are preferred because the resulting toner resin possess greater resistance to film formation on reusable imaging surfaces and resist the formation of fines under machine operation conditions. Optimum results are obtained with alpha unsaturated dicarboxylic acids including fumaric acid, maleic acid or maleic acid anhydride because maximum resistance to physical degradation of the toner as well as rapid melting properties are achieved. It is believed that the presence of the unsaturated bonds in the alpha unsaturated dicarboxylic acid reactants provides the resin molecules with a greater degree of toughness without adversely affecting the fusing and comminution characteristics. The developers of this invention contain from about 0.02 percent to about 20 percent by weight, based on the weight of the toner in the final developer mixture, of the solid hydrophobic acid metal salt of a higher fatty acid. Preferably, the developers of this invention contain from about 0.05 to about 4 percent by weight of the metal salt because maximum reduction of background deposits and image density are achieved.
Without the presence of a solid stable hydrophobic metal salt of a higher fatty acid in the developer, extremely rapid degradation of reusable imaging surfaces, untenably high background, reduced toner image density, poor toner image transfer, reduced carrier particle life, inordinate image smudging in removing gold backing of toner material from reusable imaging surfaces, and reduced electrical stability occurs. Although the initial electrostatic imaging surface potential may be reduced and abrasion resistance improved when the proportion of metal salt present is increased above about 10 percent, undesirable background deposition increases. If insufficient voltage is reduced to compensate for the presence of metal salt in excess of about 10 percent, the images begin to acquire a “washed out” appearance. It is not essential that the entire surface of each toner particle be coated with the metal salt, e.g., sufficient metal salt is present when about 10 to about 16 percent of the toner particle surfaces are coated with a metal salt. When the metal salt is dispersed rather than coated on a toner or carrier particle, proportionately more metal salt is necessary in order to maintain a sufficient quantity of the exposed salt at the surface of the toner or carrier particle. The additional amount of metal salt necessary depends to a large extent on the surface area of the developer particles, hence upon the particle diameter selected. Any suitable stable solid hydrophobic metal salt of a fatty acid having a melting point greater than about 57° C. may be employed. Optimum results are obtained when about 0.05 to about 4 percent by weight, based on the weight of the toner, of zinc stearate is available at the outer surfaces of the particles in the developing material. The developers of this invention containing zinc stearate are preferred because the resulting mixture is characterized by outstanding fusing rates, a clearness and fluidity from electrostatic imaging surfaces, greater triboelectric stability, dense toner images and increased resistance to mechanical attrition. Unexpectedly, both the fire hazard and excessive power consumption problems encountered in prior art high speed xerographic development processes are obviated when toners containing the above described polymeric esterification product and metal salt are employed. Diphenolic reactants corresponding to the formula set forth above are well known and may be prepared, for example, by reacting the alkali salts of an alkyliden or cycloalkyliden diphenol with the appropriate olefin chlorohydrin as described, for example, in U.S. Pat. 2,331,265. Another well known method for preparing the diphenolic alcohols represented by the formula above consists of the direct addition of an alkylene oxide or allylene oxide to alkyliden or cycloalkyliden diphenols. The methods of forming the polyalcohols of this invention are well known in the art and are not a subject of the present invention. When mixtures of alcoholic and phenolic hydroxyl compounds are employed to form the diphenol, the alkylene oxides react preferentially with the phenolic hydroxyl groups. Therefore, when two or more of the alkylene oxides are added to one mole of diphenol, both phenolic hydroxyl groups are substantially etherified, and the requirement in the formula set forth above that both \( n_1 \) and \( n_2 \) shall equal at least one is satisfied. However, slightly more than the stoichiometric amount of alkylene or allylene oxide is often added to produce a more flexible molecule less than about 21 because the toner resin then possesses greater resistance to film formation on reusable imaging surfaces and resist the formation of fumes under machine operation conditions. Optimum results are obtained with alpha unsaturated dicarboxylic acids including fumaric acid, maleic acid, or maleic acid anhydride because maximum resistance to physical degradation of the toner as well as rapid melting properties are achieved. Although it is not entirely clear, it is believed that the presence of the unsaturated bonds in the alpha unsaturated dicarboxylic acid reactants provides the resin molecules with a greater degree of toughness without adversely affecting the fusing and comminution characteristics.

Any suitable conventional esterification process may be employed to form the linear resins of this invention. Generally, the dihydric alcohols and dicarboxylic acids are esterified in approximately equimolar proportions. In preparing the linear toner polymers, the esterification reaction is continued until the reaction mixture has a melting point of at least about 110° F. Preferably, the resins of this invention are selected to have a melting point between about 110° F. and about 240° F.

\[
\text{HOOCR} \quad (R = \text{COOH})
\]

wherein \( R' \) represents a substituted or unsubstituted alkylene radical having from 1 to 12 carbon atoms, arylenic radical or alkylene arylene radicals having from 1 to 12 carbon atoms and \( n_2 \) is less than 2. Throughout this specification and in the appended claims the expression dicarboxylic acid is intended to include anhydrides of such acids where such anhydrides exist. Typical dicarboxylic acids include: oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, phththalic acid, mesaconic acid, homophthalic acid, isophthalic acid, terephthalic acid, o-phenyleneacetic-beta-propionic acid, itaconic acid, maleic acid, malic acid anhydrides, fumaric acid, phthalic acid anhydride, tricarboxylic acid, citraconic acid, and the like. Dicarboxylic acids having from 3 to 5 carbon atoms are preferred because the resulting toner resins possess greater resistance to film formation on reusable imaging surfaces and resist the formation of fumes under machine operation conditions. Optimum results are obtained with alpha unsaturated dicarboxylic acids including fumaric acid, maleic acid, or maleic acid anhydride because maximum resistance to physical degradation of the toner as well as rapid melting properties are achieved. Although it is not entirely clear, it is believed that the presence of the unsaturated bonds in the alpha unsaturated dicarboxylic acid reactants provides the resin molecules with a greater degree of toughness without adversely affecting the fusing and comminution characteristics.

2,2-bis(4-hydroxy isopropoxyphenyl) propane, 2,2-bis(4-hydroxy ethoxy phenyl) propane, 2,2-bis(4-hydroxy ethoxy phenyl) butane, 2,2-bis(4-hydroxy-propoxy-phenyl) propane, 2,2-bis(4-hydroxy-propoxy-phenyl) propane, 1,1-bis(4-hydroxy-propoxy-phenyl) heptane, 2,2-bis(3-methyl-4-beta-hydroxy ethoxy-phenyl) propane, 1,1-bis(4-beta-hydroxy ethoxy phenyl) cyclohexane, 2,2-bis(4-beta-hydroxy ethoxy phenyl) norbornane, 2,2-bis(4-beta-hydroxy ethoxy phenyl) norbornane, 2,2-bis(4-beta-hydroxy styryl oxophenyl) propane, the ployoxyle-ethylene mixture of isopropyliden diphenol in which both phenolic hydroxyl groups are oxynethylated and the average number of oxynethyl groups per mole is 2.6, the poloxypolynylene ether of 2-butyliden diphenol in which both the phenolic hydroxyl groups are oxynethylated and the average number of oxynpropylene groups per mole is 2.5, and the like. Diphensols wherein \( R \) represents an alkylidenic radical having from 2 to 4 carbon atoms and \( R' \) and \( R'' \) represent an alkylidenic radical having from 3 to 4 carbon atoms are preferred because greater blocking resistance, increased definition of xerographic characters and more complete transfer of toner images are achieved. Optimum results are obtained with diols in which \( R \) is isopropylidenic and \( R' \) and \( R'' \) are selected from the group consisting of propylene and butylene because the resins formed from these diols possess higher agglomeration resistance and penetrate extremely rapidly into paper receiving sheets under fusing conditions. Any suitable dicarboxylic acid may be reacted with the diols described above to form the toner resins of this invention. These acids may be substituted, unsubstituted, saturated or unsaturated. These acids have the general formula:

\[
\text{HOOCR} \quad (R = \text{COOH})
\]
for maximum fusing efficiency in high speed copying and duplicating machines. The molecular weight of the toner resins of this invention at a given melting point temperature varies considerably depending upon the activants employed. The melting point of the toner resins of this invention may be conveniently determined by any suitable method. The melting temperatures set forth in this specification are determined by means of a Fisher-Johns melting point apparatus in which each fresh toner or resin melt is brought into the tops of the metal particles having a size less than 20 mesh. Surprisingly, the polymers of this invention are highly resistant to physical degradation, film formation and impaction at relatively low molecular weights compared to conventional esters of linear polyols and dicarboxylic acids. For example, excellent results are obtained with equimolar quantities of fumaric acid and 2,2-bis(4-beta hydroxy ethoxy phenyl)-propane having a molecular weight as low as about 3,500. The molecular weight required to provide a toner resistant to film formation and impaction ranges from about 1,000 to about 60,000. As pointed out above, the toner polymers of the present invention may be made by esterification techniques well known in the art. In order to insure that the diol and dicarboxylic acid condenses to a sufficient degree to provide the desired melting point, the proportions of diol and dicarboxylic acid are so taken that a sufficient number of the resin radicals will be present in substantially stoichiometric proportions. When relatively volatile dibasic acids such as fumaric or maleic acid are employed, the reaction is carried out in an inert atmosphere at moderate temperatures and substantially atmospheric pressure during the early stages to minimize loss of a dibasic acid by volatilization. While esterification catalysts such as benzyl peroxide may be employed, it is generally preferred to carry out the reaction in the absence of a catalyst to avoid contamination of the ultimate resinous product with catalyst residue. Where a catalyst is employed, less than about 5 weight percent, based on the total weight of the reactants should be employed to avoid excessive catalyst contamination. If desired, a small amount, for example up to about 1 percent by weight, of a suitable polymerization inhibitor such as hydroquinone, pyrogallol, or the like, may be added to the charge during the esterification where the possibility of cross-linking through the acid unsaturation groups may occur.

Minor proportions of a lower alkylene glycol may also be employed with the diphenols in preparing the linear toner polymers of this invention. Typical lower alkylene glycols include: ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol and mixtures thereof. For satisfactory results, the proportions of lower alkylene glycol should remain below about 50 mole percent of the total alcohol employed in the esterification reaction. Resistance to film formation and physical degradation are greatly enhanced when the quantity of lower alkylene glycol is maintained below about 10 mole percent of the total reacting diol material.

The polymeric esterification product employed in the toners of this invention may be copolymerized or blended with one or more other thermoplastic resins if desired. When blended with another thermoplastic resin, the added resin is preferably an aromatic resin, aliphatic resin, or mixtures thereof because the resulting blend is characterized by uniformly improved consistency and high predictability of physical properties from batch to batch. Many thermoplastic resins may be blended with the resin of this invention. Typical thermoplastic resins which may be included are modified formaldehyde resins, oil modified epoxy resins, polyurethane resins, cellulosic resins, vinyl type resins and mixtures thereof. When the resin component of the toner contains an added resin, the added component should be present in an amount less than about 50 percent by weight, based on the total weight of the resin present in the toner. A relatively high percentage of the polymeric diol and dicarboxylic acid condensation product in the resinous component of the toner is preferred because a greater reduction of fusing temperatures is achieved with a given quantity of activants upon the activants employed.
ate, zinc ricinoleate, cadmium ricinoleate and mixtures thereof.

When the solid hydrophobic metal salt of a higher fatty acid is physically mixed with or applied as a coating on toner or carrier particles, rather than dispersed throughout the surface of the metal salt, a minor amount from about 0.02% to about 10% based on the weight of the toner in the final developer mixture. Optimum results are obtained with about 0.05 to about 4% of the metal salt. Although the initial electrostatic imaging surface potential may be reduced abrasion resistance improved when the proportion of metal salt present is increased above about 10%. Undesirable background deposits increase noticeably. If the charge voltage is reduced to compensate for the presence of metal salt in excess of about 10%, the images begin to acquire a "washed out" appearance. It is not essential that the entire surface of each toner particle be coated with the metal salt, e.g., sufficient metal salt is present when 10 to 16% of the toner particles containing coating may be the colorant for the toner particles. Toner colorants are well known and include, for example, carbon black, nigrosine dye, aniline blue, Calco Oil Blue, chrome yellow, ultra marine blue, Quinoline Yellow, methylene blue chloride, Monastral Blue, Malachite Green Oxalate, lamplack, Rose Bengal, Monastral Red, Sudan Black BN, and mixtures thereof. The pigment or dyes should be present in the toner in a sufficient quantity to render it highly colored so that it will form a clearly visible image on a recording member. Thus, for example, where conventional xerographic copies of typed documents are desired, the toner may comprise a black pigment such as carbon black or a black dye such as Sudan Black BN dye available from General Aniline and Film Corporation. Preferably, for high quality, the pigment or dye should be present in an amount from about 1% to about 20% by weight, based on the total weight of the colored toner. If the toner colorant employed is a dye, substantially smaller quantities of colorant may be used. The resins of this invention appear to have a surprisingly high affinity for dyes and are more easily and uniformly dyed than most conventional toner resins. Although it is not entirely clear, it is postulated that the unusually large spacing between the linear polymer molecules of the toners of this invention allow large dye molecules to uniformly penetrate and intimately mix with the resin molecules. The colorants may be mixed with the resin component prior to, during or after the resin component is polymerized. Obviously, any colorant which inhibits polymerization should be blended with the resin after the resin is formed.

The toner compositions of the present invention may be prepared by any well known toner mixing and comminution technique. For example, the ingredients may be thoroughly mixed by blending and milling the components and thereafter micropulverizing the resulting mixture. Another well known technique for forming toner particles is to spray-dry a suspension, a hot melt, or a solution of the toner composition.

When the toner mixtures of this invention are to be employed in cascade development processes, the toner should have an average particle diameter less than about 50 microns and preferably between about 5 and about 17 microns for optimum results. For use in powder cloud development methods, particle diameters of slightly less than 1 micron are preferred. Suitable coated and uncoated carrier materials for cascade and magnetic brush development are well known in the art. The carrier particles may be electrically conductive, insulating, magnetic or non-magnetic, provided that the carrier particles acquire a charge having an opposite polarity to that of the toner particles when brought in close contact with the toner particles so that the toner particles adhere to and surround the carrier particles. When a positive reproduction of the electrostatic image is desired, the carrier particle is selected such that the toner particles acquire a charge having a polarity opposite to that of the electrostatic latent image. Alternatively, if a reversal reproduction of the electrostatic image is desired, the carriers are selected so that the toner particles acquire a charge having the same polarity as that of the electrostatic latent image. Thus, the materials for the carrier particles are selected in accordance with their triboelectric properties in respect to the electroscopic toner so that when mixed or brought into mutual contact, one component of the developer is charged positively if the other component is below the first component in the triboelectric series and negatively if the other component
is above the first component in the triboelectric series. By proper selection of materials in accordance with their triboelectric effects, the polarities of their charge when mutually contacted, Xerox 813 toner particles adhere to and are coated on the surfaces of carrier particles and also adhere to that portion of the electrostatic image-bearing surfaces having a greater attraction for the toner than the carrier particles. Typical carriers include sodium chloride, ammonium chloride, aluminum potassium sulfate, chlorides of the sulfate, salt, sodium nitrate, aluminum nitrate, potassium chloride, granular zircon, granular silicon, methyl methacrylate, glass, silicon dioxide and the like. The carriers may be employed with or without a coating. Many of the foregoing and typical carriers are described by L. E. Walkup in U.S. Pat. 2,615,551; L. E. Walkup et al. in U.S. Pat. 2,638,416 and E. N. Wise in U.S. Pat. 2,618,552. An ultimate coated carrier particle diameter between about 50 microns to about 1,000 microns is preferred because the carrier particles then possess sufficient density and inertia to avoid adhesion to the electrostatic images during the cascade development process. Adherence of carrier beads to xerographic drum surfaces is undesirable because of the formation of deep scratches on the surface during the image transfer and drum cleaning steps, particularly where cleaning is accomplished by a web cleaner such as the web disclosed by W. P. Graff, Jr. et al. in U.S. Pat. 3,186,838. Also, print deletion occurs when carrier beads adhere to xerographic imaging surfaces. Generally speaking, satisfactory results are obtained when about 1 part toner is used with about 100 parts by weight of carrier.

The toner compositions of the invention may be employed to developlatent electrostatic images on any suitable electrostatic latent image-bearing surface including conventional photoc conductive surfaces. Well known photoconductive materials include vitreous selenium, organic or inorganic photoconductors embedded in a non-photoconductive matrix, organic or inorganic photoconductors embedded in a photoconductive matrix, and the like. Representative patents in which photoconductive materials are disclosed include U.S. Pat. 2,803,542 to Ullrich, U.S. Pat. 2,970,906 to Bixby, U.S. Pat. 3,121,006 to Middleton, U.S. Pat. 3,121,007 to Middleton, and U.S. Pat. 3,131,982 to Corrin.

DESCRIPTION OF PREFERRED EMBODIMENTS

The following examples further define, describe and compare methods of preparing the toner materials of the present invention and of utilizing them to develop electrostatic latent images. Parts and percentages are by weight unless otherwise indicated.

EXAMPLE I

A sample of Xerox 813 toner particles sold by the Xerox Corporation, Rochester, N.Y., is employed as a control. Copies of a standard test pattern are made with the toner in a modified 813 Xerox copying machine. The fuser temperature is regulated with a proportional temperature controller and is monitored by means of a thermocouple mounted in the center of the upper fuser plate. The fuser unit comprises plates mounted about 0.75 inch apart. The toner images on 8 inch by 13 inch copy sheets are transported through the fuser at twice the normal rate, i.e., at three inches per second. Since the standard Xerox 813 copy machine drive motor stalls and overheats when the machine is operated at twice the normal speed, a motor having twice the power output is employed. After passage through the fuser, the copy sheets are transported to a cylinder having a diameter of about 4.75 inches. A conventional 813 cleaning web is pressed against the copy sheet by a spring loaded roller under a spring tension of about 40 pounds. 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 fuser temperature is established when all the test characters are legible after an abrasion run of 5 revolutions of the abrading cylinder. The Xerox 813 toner is found to be about 600°F. Some of the copy samples are found to contain glowing embers as they emerge from the toner fuser. Further, microscopic examination of the webbed cylinder reveals considerable wear and degradation of the web. Microscopic examination of the fused toner image reveals poor penetration of the toner material into the paper surface with most of the resin material remaining above the outer surface of the paper copy sheet.

EXAMPLE II

A toner mixture is prepared comprising about 5 parts by weight of carbon black (Neo Spectra Mark II) and about 95 parts by weight of a polymeric condensation product of 2,2-bis (4-hydroxy-isopropoxy-phenyl)-propane and fumaric acid having a molecular weight of about 8,000. After melting and preliminary mixing, the composition is rubber milled to yield a uniformly dispersed composition of the carbon black in the thermoplastic resin body. The resulting mixed composition is cooled and then finely subdivided in a jet pulverizer to yield toner particles having an average particle size of about 5 to about 10 microns. About 1 part by weight of the pulverized toner particles are mixed with about 0.01 part by weight of zinc stearate particles having a particle size from about 5 to about 40 microns, and about 99 parts by weight of Xerox 813 carrier beads and substituted for the developer in the testing machine described in Example I. Under substantially identical test conditions, it is found that the original standard Xerox 813 drive motor can be used and that the minimum fuser temperature at which legible copies are obtained after an abrasion run of 5 revolutions of the abrading cylinder is about 520°F. This is a reduction of about 80°F from the fuser temperature required for the control sample of Example I. No glowing embers are observed on the copy samples as they emerge from the toner fuser. Micrograph studies of the reusable imageing surface after 10,000 cycles reveals less wear and degradation on the imaging surface than the imaging surface of Example I. Microscopic examination of the fused toner images reveals excellent penetration of the toner material into the paper surface with most of the resin material embedded below the outer surface of the paper copy sheet.

EXAMPLE III

A toner mixture is prepared comprising about 10 parts by weight of carbon black (Super Carbobar) and about 90 parts by weight of a polymeric condensation product of 2,2-bis (4-hydroxy-isopropoxy-phenyl)-propane and fumaric acid having a molecular weight of about 4,000. After melting and preliminary mixing, the composition is fed into a rubber mill and thoroughly milled to yield a uniformly dispersed composition of the carbon black in the thermoplastic resin body. The resulting mixed composition is cooled and then finely subdivided in a jet pulverizer to yield toner particles having an average particle size of about 7 to about 12 microns. About 1.5 parts by weight of the pulverized toner particles are mixed with about 0.0040 part by weight of zinc stearate having a particle size between about 5 to about 40 microns, and about 99 parts by weight of Xerox 813 carrier beads and substituted for the 813 developer in the testing machine described in Example I. Under substantially identical test conditions, it is found that the original standard Xerox 813 drive motor can be used and that the minimum fuser temperature at which legible copies are obtained after an abrasion run of 5 revolutions of the abrading cylinder is about 505°F. This is a reduction of about 95°F from the fuser temperature required for the control sample of
Example I. No glowing embers are observed on the copy samples as they emerge from the fuser. Micrograph studies of the reusable imaging surface after 10,000 cycles reveals less wear and degradation of the imaging surface than the imaging surface of Example I. Microscopic examination of the fused toner image reveals substantial wetting of the paper fibers by the resin with most of the resin material embedded below the outer surface of the paper copy sheet.

**EXAMPLE IV**

A toner mixture is prepared comprising about 7 parts by weight of carbon black (Super Carbobar) and about 93 parts by weight of a polymeric condensation product of 2,2-bis (4-beta hydroxy ethoxy phenyl) -propene and fumaric acid having a molecular weight of about 5,000. After melting and preliminary mixing, the composition is fed into a rubber mill and thoroughly milled to yield a uniformly dispersed composition of the carbon black in the thermoplastic resin body. The resulting mixed composition is cooled and then finely subdivided in a jet pulverizer to yield toner particles having an average particle size of about 10 to about 15 microns. About 1 part by weight of the pulverized toner particles are mixed with about 0.015 part by weight of cobalt palmitate having a particle size range between about 0.5 to about 30 microns and about 99 parts by weight of 813 Xerox carrier beads and substituted for the 813 developer in the testing machine described in Example I. Under substantially identical test conditions, it is found that the original standard Xerox 813 drive motor can be employed and that the minimum fuser temperature at which legible copies are obtained after an abrasion run of 5 revolutions of the abrading cylinder is about 500° F. This is a reduction of 50° F. from the fuser temperature required for the control sample of Example I. No glowing embers are observed on the copy sheet samples as they emerge from the fuser. Micrograph studies of the imaging surface after 10,000 cycles reveals less wear and degradation of the surface than the imaging surface of Example I. Microscopic examination of the fused toner image reveals very good wetting of the paper by the toner with most of the resin material embedded below the outer surface of the paper copy sheet.

**EXAMPLE V**

A toner mixture is prepared comprising about 5 parts by weight of Sudan Black-BN dye and about 95 parts by weight of a polymeric condensation product of 2,2-bis (3-methyl-4-beta-hydroxy ethoxy phenyl) -propene and maleic anhydride having a molecular weight of about 2,000. After melting and preliminary mixing, the composition is fed into a rubber mill and thoroughly milled to yield a uniformly dispersed composition of the dye in the thermoplastic resin body. The resulting mixed composition is cooled and then finely subdivided in a jet pulverizer to yield toner particles having an average particle size of about 6 to about 9 microns. About 2 parts by weight of the pulverized toner particles are mixed with about 0.015 part by weight of iron oxide particles having a size range from about 5 to about 40 microns and about 99 parts by weight of 813 Xerox carrier beads and substituted for the 813 developer in the testing machine described in Example I. Under substantially identical test conditions, it is found that the original standard Xerox 813 drive motor can be employed and that the minimum fuser temperature at which legible copies are obtained after an abrasion run of 5 revolutions of the abrading cylinder is about 500° F. This is a reduction of 50° F. from the fuser temperature required for the control sample of Example I. No glowing embers are observed on the copy sheet samples as they emerge from the fuser. Micrograph studies of the imaging surface after 5,000 cycles reveals less wear and degradation of the surface than the imaging surface of Example I. Microscopic examination of the fused toner image reveals very good wetting of the paper by the toner with most of the resin material embedded below the outer surface of the paper copy sheet.

**EXAMPLE VI**

A toner mixture is prepared comprising about 5 parts by weight of Sudan Black-BN dye, 2 parts by weight carbon black (Neo Spectra Mark II), and about 95 parts by weight of a polymeric condensation product of 2,2-bis (4-hydroxy isoproxy phenyl) -propene, ethylene glycol and itaconic acid having a molecular weight of about 1,500. After melting and preliminary mixing, the composition is fed into a rubber mill and thoroughly milled to yield a uniformly dispersed composition of the dye in the thermoplastic resin body. The resulting mixed composition is cooled and then finely subdivided in a jet pulverizer to yield toner particles having an average particle size of about 6 to about 9 microns. About 2 parts by weight of the pulverized toner particles are mixed with about 0.015 part by weight of iron oxide particles having a size range from about 5 to about 40 microns and about 99 parts by weight of 813 Xerox carrier beads and substituted for the 813 developer in the testing machine described in Example I. Under substantially identical test conditions, it is found that the original standard Xerox 813 drive motor can be used and that the minimum fuser temperature at which legible copies are obtained after an abrasion run of 5 revolutions of the abrading cylinder is about 500° F. This is a reduction of 50° F. from the fuser temperature required for the control sample of Example I. No glowing embers are observed on the copy sheet samples as they emerge from the fuser. Micrograph studies of the imaging surface after 5,000 cycles reveals less wear and degradation of the surface than the imaging surface of Example I. Microscopic examination of the fused toner image reveals very good wetting of the paper by the toner with most of the resin material embedded below the outer surface of the paper copy sheet.

**EXAMPLE VII**

A toner mixture is prepared comprising about 5 parts by weight of Sudan Black-BN dye, 2 parts by weight carbon black (Neo Spectra Mark II), and about 95 parts by weight of a polymeric condensation product of 2,2-bis (4-beta-hydroxy ethoxy phenyl) -propene, ethylene glycol and itaconic acid having a molecular weight of about 2,200. After melting and preliminary mixing, the composition is fed into a rubber mill and thoroughly milled to yield a uniformly dispersed composition of the dye in the thermoplastic resin body. The resulting mixed composition is cooled and then finely subdivided in a jet pulverizer to yield toner particles having an average particle size of about 6 to about 9 microns. About 2 parts by weight of the pulverized toner particles are mixed with about 0.015 part by weight of iron oxide particles having a size range from about 0.60 to about 35 microns, and about 99 parts by weight of 813 Xerox carrier beads and substituted for the 813 developer in the testing machine described in Example I. Under substantially identical test conditions, it is found that the original standard Xerox 813 drive motor can be employed and that the minimum fuser temperature at which legible copies are obtained after an abrasion run of 5 revolutions of the abrading cylinder is about 500° F. This is a reduction of 50° F. from the fuser temperature required for the control sample of Example I. No glowing embers are observed on the copy sheet samples as they emerge from the fuser. Micrograph studies of the imaging surface after 10,000 cycles reveals less wear and degradation of the surface than the imaging surface of Example I. Microscopic examination of the fused toner image reveals very good wetting of the paper by the toner with most of the resin material embedded below the outer surface of the paper copy sheet.

**EXAMPLE VIII**

About 1.5 parts by weight of the pulverized toner particles of the type described in Example III are mixed with about 0.0040 part by weight of lead stearate particles having a particle size between about 2 to about 30
microns, and about 99 parts by weight of glass beads having an average diameter of about 300 microns and coated with a silicone terpolymer reaction product of butyl methacrylate, styrene and vinyl trioxysilane and substituted for the 813 developer in the testing machine described in Example I. Under substantially identical test conditions, it is found that the minimum fusor temperature at which legible copies are obtained after an abrasion run of 5 revolutions of the abrading cylinder is about 50°C. This is a reduction of about 10°C from the fusor temperature required for the control sample of Example I. No glowing embers are observed on the copy sheet samples as they emerge from the fusor. Micrograph studies of the reusable imaging surface after 5,000 cycles reveals less wear and degradation of the surface than the imaging surface of Example I. Microscopic examination of the dense fused toner image reveals substantial wetting of the paper fibers by the resin with most of the resin material embedded below the outer surface of the paper copy sheet.

EXAMPLE IX

About 2 parts by weight of the pulverized toner particles of the type described in Example IV are mixed with about 0.002 part by weight of zinc ricinoleate particles having a particle size between about 0.2 to about 33 microns and about 99 parts by weight of polyvinyl alcohol having an average diameter of about 600 microns and coated with ethyl cellulose. The resulting developer is substituted for the Xerox 813 developer in the testing machine described in Example I. Under substantially identical conditions, it is found that the minimum fusor temperature at which legible copies are obtained after an abrasion run of 5 revolutions of the abrading cylinder and toner penetration into the paper copy sheet surfaces are substantially the same as the results recorded with the toner sample of Example IV. No glowing embers are observed on the copy samples as they emerge from the fusor. Micrograph studies of the reusable imaging surface after 5,000 cycles reveals less wear and degradation than the imaging surface of Example I.

EXAMPLE X

The Xerox 813 toner described in Example I is tested in a Fisher-Jones Melting Apparatus for its tack temperature and its fluid temperature. The tack temperature is that temperature at which agglomeration of the toner particles is first observed. The fluid temperature is that temperature at which the entire toner sample is entirely fluid. The Xerox 813 toner tack temperature is found to be about 158°F and the fluid temperature about 226°F. Thus, the difference between the tack and fluid temperature is about 61°F.

EXAMPLE XI

A sample of toner particles of the type described in Example II is tested for its tack and fluid temperature in substantially the same manner as that described in Example X. The tack temperature is found to be about 158°F and the fluid temperature about 194°F. The difference between the tack and fluid temperatures is about 36°F, which is almost half that of the Example X toner. Thus the smaller difference between the tack and fluid temperatures of the tone of Example I is considerably less than the difference found in testing the toner of Example IX. This smaller difference allows the molecular weight of the resin of Example II to be adjusted to provide a lower fusing temperature than that of the Xerox 813 toner without encountering toner blocking during storage or use due to the tackiness of the toner.

EXAMPLE XII

A sample of toner particles of the type described in Example III is tested for its tack and fluid temperature in substantially the same manner as that described in Example X. The tack temperature is found to be about 147°F and the fluid temperature about 180°F. The difference between the tack and fluid temperatures is about 33°F, which is approximately half that of the Example X toner.

EXAMPLE XIII

A sample of toner particles of the type described in Example IV is tested for its tack and fluid temperature in substantially the same manner as that described in Example X. The tack temperature is found to be about 144°F and the fluid temperature about 185°F. The difference between the tack and fluid temperatures is about 41°F. Thus, the smaller difference between the tack and fluid temperatures of the toner of Example IV is considerably less than the difference found in testing the toner of Example X.

EXAMPLE XIV

A control toner mixture is prepared comprising about 5 parts by weight of carbon black and about 90 parts by weight of a polymeric esterification product of a linear alcohol, hexamethylene glycol, and a dicarboxylic acid, sebacic acid. This polymer, hexamethylene sebacate, has a molecular weight of about 20,000 and a melting range of about 160 to 220°F. After melting and preliminary mixing, the composition is fed into a rubber mill and thoroughly milled to yield a uniformly dispersed composition of the carbon black in the thermoplastic resin body. The resulting mixed composition is cooled and then finely subdivided in a jet pulverizer to yield toner particles having an average particle size of about 7 to about 12 microns. About 1 part by weight of the pulverized toner particles are mixed with about 99 parts by weight of Xerox 813 carrier beads and substituted for the 813 developer in the testing machine described in Example I. The toner images after fusing are extremely faint, poorly defined and almost illegible. After about 70 imaging cycles, a heavy film of the toner is found on the surface of the modified Xerox 813 xerographic drum.

EXAMPLE XV

A toner mixture is prepared comprising about 5 parts by weight of carbon black, about 75 parts by weight of a polymeric condensation product of 2,2-bis (4-hydroxyisopropoxy phenyl)-propane and furamic acid having a molecular weight of about 8,000 and about 20 parts by weight of sucrose benzoate. After melting and preliminary mixing, the composition is fed into a rubber mill and thoroughly milled to yield a uniformly dispersed composition of the carbon black in the thermoplastic resin body. The resulting mixed composition is cooled and then finely subdivided in a jet pulverizer to yield toner particles having an average particle size of about 5 to about 10 microns. About 1 part by weight of the pulverized toner particles are mixed with about 0.0025 part by weight of zinc stearate particles having a particle size of about 0.5 to about 45 microns and about 99 parts by weight of uncoated glass carrier beads and substituted for the developer in the testing machine described in Example XIV. Under substantially identical test conditions, the resulting toner images are highly legible and very dense. A negligible haze is found on the surface of the xerographic drum.

EXAMPLE XVI

A toner mixture is prepared comprising about 7 parts by weight of carbon black and about 93 parts by weight of a polymeric condensation product of 2,2-bis (4-beta hydroxy ethoxy phenyl)-propane and furamic acid having a molecular weight of about 5,000. After melting and preliminary mixing, the composition is fed into a rubber mill and thoroughly milled to yield a uniformly dispersed composition of the carbon black in the thermoplastic resin body. The resulting mixed composition is cooled and then finely subdivided in a jet pulverizer to yield toner particles having an average particle size of about 10 to about 15 microns. About 1 part by weight of the pul-
3,590,000

verized toner particles are mixed with about 0.01 part by weight of zinc stearate particles having a size range from about 0.5 to about 45 microns and about 99 parts by weight of 813 Xerox carrier beads and substituted for the 813 developer in the testing machine described in Example I. Under substantially identical test conditions, the resulting toner images are dense with excellent edge definition. An almost imperceptible haze of toner material is found on the surface of the xerographic drum.

EXAMPLE XVII

A control sample containing one part colored preformed toner particles of the type described in Example III having an average particle size of about 5 to about 10 microns is mixed with about 99 parts of coated glass beads having an average particle size of about 250 microns and then cascaded across an electrostatic image-bearing drum surface. The developed image is then transferred by electrostatic means to a sheet of paper whereon it is fused by heat. The residual powder is removed from the electrostatic imaging surface by a cleaning web of the type disclosed by W. P. Goff, Jr., et al. in U.S. Pat. 3,186,838. After the copying process is repeated 25,000 times, the copies and electrostatic image-bearing surface are examined for quality and wear, respectively. The copies possess sharp line contrast and minimal background deposition. However, an examination of the imaging surface reveals the effects of considerable wear.

EXAMPLE XVIII

About 0.03 part of zinc stearate having a particle size distribution from about 0.75 micron to about 40 microns is gently folded into one part of a colored preformed toner particle of the type described in Example XVII. The resulting developer mixture is then thoroughly mixed in a Szegvari attritor for about 10 minutes. The developing procedure of Example XVIII is repeated with a new drum and with the foregoing mixed milled mixture substituted for the toner of Example XVII at a relative humidity of about 50 percent of 70° F. and a relative humidity of 80 percent at 80° F. Copies prepared with the milled sample possess higher density solid area coverage than copies prepared with the control sample. Further, micrograph studies of the electrostatic image-bearing surface reveals lower wear than on the image-bearing surface of Example XVIII. Considerably less toner is necessary to drive the drum when the stearate additive is employed and a lower voltage is required to transfer the toner images to a receiving sheet.

EXAMPLE XIX

About 0.025 part zinc stearate having a particle size distribution from about 0.75 micron to about 40 microns is gently folded into about 10 parts of a colored preformed toner particle of the type described in Example III. The resulting mixture is then tumbled in a sealed container for 15 minutes. About one part of the tumbled mixture is mixed with 99 parts of carrier beads having an average particle size of about 250 microns. The resulting developer mixture is employed in a cascade developing process as described in Example XVIII at a relative humidity of 50 percent at 70° F. and at a relative humidity of 80 percent at 80° F. The resulting fused toner images possess both higher density and better image quality than the images obtained in Example XVIII.

The expression “developing material” as employed herein is intended to include electroscopic toner material or combinations of toner material and carrier material.

Although specific materials and conditions are set forth in the foregoing examples, these are merely intended as illustrations of the present invention. Various other suitable toner resin, additives, colorants, and other components, such as those listed above may be substituted for those in the examples with similar results. Other materials such as plasticizers may also be added to the toner to sensitize, synergize, or otherwise improve the fusing properties or other desirable properties of the system.

Other modifications of the present invention will occur to those skilled in the art upon a reading of the present disclosure. These are intended to be included within the scope of this invention.

What is claimed is:

1. A solid xerographic developer material comprising particles, said particles including finely divided toner material having a particle size range of about 30 microns and a melting point of at least about 110° F., said toner material comprising a colorant selected from the group consisting of pigments, dyes and mixtures thereof and a resin consisting essentially of a polymeric esterification product of a dicarboxylic acid and a diol comprising a diphenol; and from about 0.02% to about 20%, by weight, based on the weight of said toner material, of at least one solid, stable hydrophobic metal salt of a fatty acid available at external surfaces of said particles.

2. A xerographic developer material according to claim 1 wherein said colorant is pigmented in an amount of from about 1 to about 20%, by weight, of said toner material.

3. A xerographic developer material according to claim 1 wherein said resin is a polymeric esterification product of from about equimolar quantities of a dicarboxylic acid and a diol comprising a diphenol.

4. A xerographic developer material according to claim 1 wherein said diphenol has the general structure

\[ \text{HOO}_2\text{C}’’\text{R’’}\text{COOH} \]

and anhydrides thereof wherein R’’’ is selected from the group consisting of allyl radicals having from 1 to 12 carbon atoms, alkylene radicals having from 1 to 12 carbon atoms and cyclo-alkyl radicals having from 3 to 12 carbon atoms; R’ and R” are selected from the group consisting of allyl radicals having from 1 to 12 carbon atoms and alkylene radicals having from 8 to 12 carbon atoms; X and X’ are selected from the group consisting of hydrogen and alkyl radicals having from 1 to 4 carbon atoms; and \( n_1 \) and \( n_2 \) are each at least 1 and the average sum of \( n_1 \) and \( n_2 \) is less than 2.

5. A xerographic developer material according to claim 1 wherein said dicarboxylic acid is selected from the group consisting of acids having the general formula

\[ \text{HOC}’’’\text{R’’’}\text{COOH} \]

and anhydrides thereof wherein R’’’ is selected from the group consisting of allyl radicals having from 1 to 12 carbon atoms, alkylene radicals having from 1 to 12 carbon atoms, acrylly radicals and alkylene acrylic radicals having from 10 to 12 carbon atoms and \( n_2 \) is less than 2.

6. A xerographic developer material according to claim 1 wherein said polymeric esterification product is a condensation product of 2,2 bis (4-hydroxy-isopropoxy-phenyl)-propane and fumaric acid.

7. A xerographic developer material according to claim 1 wherein said polymeric esterification product is a condensation product of 2,2 bis (4-hydroxy-isopropoxy-phenyl)-propane and 2,2 dimethyl fumaric acid.

8. A xerographic developer material according to claim 1 wherein said polymeric esterification product is a condensation reaction product of 2,2 bis (4-hydroxy-butoxy-phenyl)-propane and fumaric acid.

9. A xerographic developer material according to claim 1 wherein said polymeric esterification product is a condensation product of 2,2 bis (4-hydroxy-isoxy-phenyl)-propane and 2,2-dimethyl fumaric acid.

10. A xerographic developer material according to claim 1 wherein said polymeric esterification product is a condensation product of 2,2 bis (4-hydroxy-ethoxy-phenyl)-propane and fumaric acid.
A xerographic developer material according to claim 1 wherein said developer material includes carrier beads having an average particle size from about 50 microns to about 1,000 microns.

A xerographic developer material according to claim 1 wherein said solid hydrophobic metal salt of a fatty acid is zinc stearate.

A xerographic developer material according to claim 1 wherein less than about 50 mole percent of said diol is a lower alkylene glycol.

A xerographic developer material according to claim 1 wherein said metal salt of a fatty acid has a melting point greater than about 57°C and is available from about 10 percent to about 16 percent of the external surfaces of said toner particles.

A treated xerographic toner comprising toner particles, said toner particles having a melting point of at least about 110°F, said toner comprising a colorant selected from the group consisting of pigments, dyes and mixtures thereof and a resin consisting essentially of a polymeric esterification product of a diol comprising a diphenol having the general structure:

\[
H(\text{OR}')(\text{OR})_2\text{R}^{IV} \text{R}^{IV} \text{X} \text{R}^{IV} \text{X'} \text{O}(\text{OR}')(\text{OR})_2\text{H}
\]

wherein \( R \) is selected from the group consisting of alkylene radicals having from 2 to 12 carbon atoms, alkylidene radicals having from 1 to 12 carbon atoms and cycloalkylidene radicals having from 3 to 12 carbon atoms; \( R' \) and \( R'' \) are selected from the group consisting of alkylene radicals having from 2 to 12 carbon atoms and arylene radicals having from 8 to 12 carbon atoms; \( X \) and \( X' \) are selected from the group consisting of hydrogen and alkyl radicals having from 1 to 4 carbon atoms; and \( n_1 \) and \( n_2 \) are each at least 1 and the average sum of \( n_1 \) and \( n_2 \) is less than 21 and a dicarboxylic acid selected from the group consisting of acids having the general formula:

\[
\text{HOOCR''}_2\text{n}_2\text{COOH}
\]

and anhydrides thereof wherein \( R'' \) is selected from the group consisting of alkylene radicals having from 2 to 12 carbon atoms, alkylidene radicals having from 1 to 12 carbon atoms and cycloalkylidene radicals having from 3 to 12 carbon atoms; \( R' \) and \( R'' \) are selected from the group consisting of alkylene radicals having from 2 to 12 carbon atoms and arylene radicals having from 8 to 12 carbon atoms; \( X \) and \( X' \) are selected from the group consisting of hydrogen and alkyl radicals having from 1 to 4 carbon atoms; and \( n_1 \) and \( n_2 \) are each at least 1 and the average sum of \( n_1 \) and \( n_2 \) is less than 21 and a dicarboxylic acid selected from the group consisting of acids having the general formula:

\[
\text{HOOCR''}_2\text{n}_2\text{COOH}
\]

and anhydrides thereof wherein \( R'' \) is selected from the group consisting of alkylidene radicals having from 1 to 12 carbon atoms, alkylidene radicals having from 1 to 12 carbon atoms and cycloalkylidene radicals having from 3 to 12 carbon atoms; \( R' \) and \( R'' \) are selected from the group consisting of alkylene radicals having from 2 to 12 carbon atoms and arylene radicals having from 8 to 12 carbon atoms; \( X \) and \( X' \) are selected from the group consisting of hydrogen and alkyl radicals having from 1 to 4 carbon atoms; and \( n_1 \) and \( n_2 \) are each at least 1 and the average sum of \( n_1 \) and \( n_2 \) is less than 21 and a dicarboxylic acid selected from the group consisting of acids having the general formula:

\[
\text{HOOCR''}_2\text{n}_2\text{COOH}
\]

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