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Azar et al.

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[54] **PRESSURE FIXABLE TONER**

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[58] **Field of Search** ..... 252/62.1 P

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[57] **ABSTRACT**

Pressure and heat/pressure fixable encapsulated electrostatographic toners comprising plasticized adhesive, soft solid core materials encapsulated in a polymeric shell material. Developer compositions employing the encapsulated toners and methods of forming visible electrostatographic toner images are also disclosed.

2 Claims, No Drawings

PRESSURE FIXABLE TONER

BACKGROUND OF THE INVENTION

This invention relates to electrostatography, and more particularly, to improved plasticized encapsulated electrostatographic developing materials and the use thereof.

The formation and development of images on the surface of photoconductive materials by electrostatographic means is well known. The basic electrostatographic process, as taught by C.F. Carlson in U.S. Pat. No. 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 electrostatic latent 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 electrostatic latent 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 as by heat. In such case, the toner must generally be heated to a temperature at which the toner flows in order to effect fusing of the toner to the support medium. 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 if 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 electrostatic latent image to be developed. One development technique, as disclosed by N. Wise in U.S. Pat. No. 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 discharged 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. No. 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 brushlike 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. No. 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 electrostatic latent 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. No. 3,166,432 may be used where suitable.

Although some of the foregoing development techniques are employed commercially today, the most widely used commercial electrostatographic 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. No. 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.

The toners employed in the art are generally fixed to a support medium by the application of heat and, therefore, such toners must be heated to a temperature at which the toner flows in order to effect fusing of the toner to the support medium. The fusion technique, although highly successful, has some disadvantages; namely, such a technique has not been readily adaptable to high speed machines as a result of the time or energy required to raise the temperature of the toner to a temperature at which the toner can be fused to the support medium. 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. 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, toners made from low melting, usually low mo-

lecular weight resins 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, the low melting toners tend to form tacky images on the copy sheet which are easily smudged and often offset to other adjacent sheets. Further, the low melting toners become tacky at temperatures that may be encountered in storage or in the high speed machines. This usually causes "blocking" or caking of the toner or developer in storage and in the machine and poor or erratic dispensing prior to and during machine operation. Additionally, these materials are often extremely difficult or even impossible to comminute in conventional grinding apparatus because they become tacky at the temperatures attained during the grinding operation. 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 triboelectric 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 electrostatographic 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 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 of the carrier particles. The gradual accumulationn 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 electrostatographic imaging surfaces accelerates mutual deterioration of these components. In addition, both filming of reusable photoconductor surfaces and impaction contribute to the phenomenon known as "bead sticking" which is the adherence of carrier beads to reusable photoconductor surfaces. When this occurs, the rubbing of the carrier beads across the photoconductor surface during cleaning operations beads to scratching and abrasion of the reusable photoconductor surface. Replacement of carriers and electrostatic image bearing surfaces is expensive and time consuming. Electrostatographic 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 electrostatic latent image are usually rewarded with an undesirable increase in background deposits.

Another disadvantage of copying machines that utilize heat to fix the thermoplastic toner materials to the image support medium is that the machines generally do not function properly immediately after their idle hours. That is, it takes a certain amount of time until the temperature of the heating system reaches the operating temperature. Therefore, it is usually necessary to maintain the temperature of the heating system at about its operating temperature in order that the machine can operate satisfactorily shortly after it is turned on. This obviously means that heat energy is constantly lost while the machine is idle.

The toner particles are usually thermoplastic resins selected to have melting points significantly above any ambient temperatures that might be encountered during electrostatic deposition. In addition to the developing powder or toner materials described in U.S. Pat. No. 2,297,691, a number of additional toner materials have been developed especially for use in the newer development techniques including the cascade technique described above. Generally speaking, these new toner materials have comprised various improved resins mixed with different pigments such as carbon black. Some exemplary patents along this line include U.S. Pat. No. 2,659,670 to Copley which describes a toner resin of rosinmodified phenolformaledhyde, U.S. Reissue No. 25,136 to Carlson which describes an electrostatographic toner employing a resin of polymerized styrene and U.S. Pat. No. 3,079,342 to Insalaco describing a plasticized copolymer resin in which the comonomers are styrene and a methacrylate selected from the group of butyl, isobutyl, ethyl, propyl, and isopropyl.

In the past, these toners have generally been prepared by thoroughly mixing a heat softened resin and colorant to form a uniform dispersion as by blending these ingredients in a rubber mill or the like and then pulverizing this material after cooling to form it into small particles. Although toners manufactured by this technique have resulted in some very excellent toner, they do tend to have certain shortcomings. For example, the toners generally have a rather wide range of particle sizes. That is, even though the average toner particle size made according to this technique generally ranges between about 5 and 10 microns, individual particles ranging from submicron in size to above 20 microns are not infrequently produced. In addition, toner produced by this technique imposes certain limitations upon the material selected for the toner because the colored resin must be sufficiently friable so that it can be pulverized at an economically feasible rate of production. The problem which arises from this requirement is that when the colored resin is sufficiently friable for really high speed pulverizing, it tends to form even a wider range of particle sizes during pulverization including relatively large percentages of fines and is frequently subject to even further pulverization or powdering when it is employed for developing in electrostatographic imaging apparatus. All other requirements of electrostatographic developers or toners including the requirements that they be stable in storage, nonagglomerative, have the proper triboelectric properties for developing and have a low melting point for heat fusing are only compounded by the additional requirements imposed by this toner forming process. Some de-

veloper materials such as those containing toner particles made from low molecular weight resins though possessing desirable properties such as proper triboelectric characteristics, are unsuitable because they tend to cake, bridge and agglomerate during handling and storage.

Of interest as electrostatographic developer materials are the pressure fixable toner materials because of their very low energy requirements. However, the toner requirements for good machine performance tend to be diametrically opposed to the requirements for pressure fixing. That is, low toner impaction requires high toner softening temperature and good mechanical strength while pressure fixing requires softening and viscous flow at room temperature. In addition, one of the problems with pressure fixable toners is the need to gently handle these materials prior to pressure fusion to paper or other suitable support medium so that these materials will not prefuse and cause impaction in the development chamber. A balance must generally be made between a material which will pressure fix onto paper at low pressure but yet not impact in the development chamber. A major cause of such prefusion is the abrasive action of the tumbling carrier beads on the toner both in normal cascade development and magnetic brush development.

The production of an encapsulated electrostatographic toner material which can be pressure fixed would be desirable and advantageous since unencapsulated materials which undergo cold flow tend to form tacky images on the copy sheet which often offset to other adjacent sheets. Toner particles containing unencapsulated materials which undergo cold flow tend to bridge, cake and block during production and in the shipping container as well as in the electrostatographic imaging machine. Also, the toner material should be capable of accepting a charge of the correct polarity such as when brought into rubbing contact with the surface of carrier materials in cascade, magnetic brush or touchdown development systems. Some toner materials which possess many properties which would be desirable in electrostatographic toners dispense poorly and cannot be used in automatic copying and duplicating machines. Other toners dispense well but form images which are characterized by low density, poor resolution, or high background. Further, some toners are unsuitable for processes where electrostatic transfer is employed.

A useful form of liquid phase separation from aqueous media is known as coacervation and is exemplified in U.S. Pat. Nos. 2,800,457 and 2,800,458 to Green. However, toner materials obtained by this method such as those comprising encapsulated inks are generally fragile, their shells are loose after fixing and tend to cause smearing of the developed image. In addition, such toner materials generally have poor electrostatographic properties since the encapsulated contents tend to diffuse through the shell material leading to alteration of triboelectric properties. Further, broken liquid core materials adversely affect copy quality due to vertical and lateral bleeding resulting in poor resolution. Other patents such as U.S. Pat. Nos. 3,080,250 and 3,386,822 disclose capsules containing solvents which tackify some portion of the toner and help to fix the image. However, such patented materials are encapsulated liquids and once the capsule is crushed, the contents will flow perceptively with little or no applied stress and because of the solvent, the presence of vapors is usually undesirable.

Since most toner 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 impaction resistant toner materials.

It is another object of this invention to provide a toner which can be fused at higher rates with less heat energy.

It is another object of this invention to provide a toner which is triboelectrically stable.

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 electrostatographic imaging surfaces.

It is another object of this invention to provide a toner which reduces mechanical abrasion of electrostatographic 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 transferrable from an electrostatographic 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 which can be fused at higher rates with less pressure.

It is another object of this invention to provide an encapsulated toner containing a core material which will flow perceptively only under significant applied stress and have sufficient cohesive strength to form a good bond between the capsule and an image substrate.

It is another object of this invention to provide an encapsulated toner containing a core material capable of improved penetration into a support medium.

It is another object of this invention to provide an encapsulated toner capable of maintaining improved mechanical strength of the fixed image.

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 above objects and others are accomplished by providing an electrostatographic toner comprising adhesive, soft solid polymeric core materials containing a colorant and a plasticizer encapsulated in a polymeric shell material. The pressure fixable plasticized encapsulated toners of this invention include any encapsu-

lated toner in which the polymeric core material is an adhesive soft solid at ambient temperature or becomes an adhesive soft solid when heated to a temperature between about 70°F. and about 250°F. The term adhesive soft solid is intended to include any material showing no perceptible flow under slight stress in a short observation period, but showing significant flow under large applied stresses and which is capable of forming a strong adhesive bond. The encapsulated pressure fixable plasticized toners of this invention include electrostatographic encapsulated toners containing a cold flowable adhesive polymeric core material. Thus, polymeric core materials having a viscosity at a shear rate of about 75 sec^{-1} of between about 5×10^4 and about 10^8 poise at ambient temperature and a glass transition temperature (Tg) below about 30°C. may be employed in the encapsulated toners of this invention which are pressure fixable without the assistance of heat. In addition, polymeric core materials having a viscosity at a shear rate of about 75 sec^{-1} of between about 5×10^4 and about 10^8 poise at the temperature of a pressure fixing device and a glass transition temperature below or not more than a few degrees above the temperature of a pressure fixing device may be employed in the encapsulated toners of this invention. Thus, polymeric core materials having a higher glass transition temperature or a higher viscosity at ambient temperature may be used where the encapsulated toners of this invention are fixed using a combination of pressure and heat. For example, where a heat assisted pressure fixing mode is employed in which one roll, typically a steel roll, is heated to about 45°C., polymeric core materials having a viscosity between about 5×10^4 and about 10^8 poise at about 45°C. may be employed. Where the polymeric core material has more than one detectable glass transition temperature, such as when it contains two or more phases, only one glass transition temperature has to be below the temperature conditions given above. In some cases, it is advantageous to use polymeric core materials which are shear sensitive, that is, those which exhibit distinctly different viscosities depending on the effective shear rate. With shear sensitive polymeric core materials, the viscosity at very low shear rates may be much higher than the range given above. However, at the shear rate occuring in the pressure fixing device used, the viscosity should be below about 10^8 poise.

In selecting a plasticizer for the core material, it is generally desirable to select a material compatible with the core material but incompatible with the wall material. This selection allows the plasticizer to blend with and concentrate in the core but not with the wall of the processed toner. Generally, plasticizer in the matrix would be detrimental to the surface properties of the toner, especially with respect to its triboelectric properties and blocking temperature. Plasticizers are used to effectively reduce the core viscosity of the encapsulated toners of this invention. It has been found that the degree of fix increases as the viscosity of the core material decreases. Since viscosity is the predominant property influencing fix, the addition of a plasticizer to the core material greatly enhances the degree of fix for the encapsulated toners of this invention. Thus, in accordance with this invention, a plasticizer is used to adjust the viscosity of the core material and consequently the fixing properties of the encapsulated toners of this invention. In addition, it has been found that the plasticizer for the core material improves the penetration of the toners of this invention into a support medium such as paper and yet provides a fixed image having excellent mechanical strength. This is evidenced by the finding that the plasticized encapsulated toners of this invention provide a degree of fix significantly greater than their nonplasticized counterparts as measured in abrasion tests on prints fixed at various pressures.

Suitable polymeric shell materials generally have a viscosity higher than the polymeric core materials and usually are materials which will not flow at moderate pressures and temperatures likely to be encountered during storage. Thus, amorphous shell materials having a glass transition temperature above about 45°C. and crystalline shell materials having a melting point above about 45°C. may be employed in the encapsulated toners of this invention. Where the shell materials exhibit more than one glass transition temperature or melting point, they generally will have at least one glass transition temperature above about 45°C. or a melting point above about 45°C., and the other glass transition temperature or melting point may be above this temperature. It is generally preferable for the shell materials to be brittle and somewhat friable because these properties permit facile and complete rupturing of the encapsulated toners to thereby release the adhesive core materials. However, for some applications, it is preferable to employ shell materials which are tough and less rigid under fixing conditions. That is, the shell material may exhibit slight flow under applied pressures at fixing temperatures. This type of polymeric shell materials is particularly useful when employing both heat and pressure for fixing the toner image. Suitable shell materials embrace a very wide range of rheological properties, since variations in the properties of the shell material can to a large extent be compensated for by adjustment of the shell thickness. In addition, the properties of suitable shell materials depend on the properties of the polymeric core material employed. Thus, the combination of the modulus of elasticity of the shell material and the shell thickness is adjusted to compensate for the viscosity of the polymeric core material used so that the shell will fracture if brittle, or rupture if ductile, under the fixing conditions of temperature and pressure employed. Thus, shell materials having a modulus of elasticity of above about 100 psi and a compressive strength of above about 500 psi provide satisfactory results. However, shell materials having a modulus of elasticity of above about 1000 psi and a compressive strength of above about 2000 psi are preferred because the resulting encapsulated toner particles provide enhanced fixing properties and freedom from impaction. Thus, shell materials such as polystyrenes, polycarbonates, and the reaction products of dimer acids with linear diamines are some of the preferred shell materials.

It has been found that there is a correlation between the glass transition temperature of the polymeric core material and the pressure fixability of the encapsulated toners of this invention. That is, the fixability of these encapsulated toners generally improves as the Tg of the polymeric core material decreases. It is postulated that the observed effect of a lower Tg is probably due to its effect on viscosity. A polymeric core material Tg below the fixing temperature is apparently a necessary condition for fixing since the flow or viscosity requirements for the core cannot be met above the Tg. Conversely, it seems improbable that a low Tg per se, without a concomitant reduction in viscosity, will improve the pres-

sure fixability. As to the desirability of a high molecular weight polymeric core material, it has been postulated that a monomeric or oligomeric core material would have too low a cohesive strength to give a good fix. However, differences in fix may be attributed to the effect of core viscosity rather than to an effect of molecular weight on cohesive strength.

In addition, it has been found that there is a reasonably good correlation between the Tg of the polymeric shell material and the toner blocking temperature. Thus, where the ratio of polymeric core material to shell material is approximately 1:1, the blocking temperature of the toner corresponds approximately to the Tg of the shell material. Crushability and pressure fixability examinations indicate that a higher molecular weight, and presumably higher strength, shell material for a given shell material such as polystyrene provides a stronger, that is, less easily crushed encapsulated toner. There is also evidence that a higher polymeric core/shell ratio provides better fixing properties, but its effect on toner crushability is indeterminate. It appears that toner crushability and fixing are affected in the same manner but in different degrees by changes in the wall and core materials as well as the core/wall ratio. In changing the wall material from low molecular weight polystyrene to the higher molecular weight polystyrenes with similar core material, or decreasing the core: wall ratio to 1:1, the fix is generally reduced but not to the extent that the crush strength is increased. Crushability measurements on encapsulated toners with relatively fluid cores agree well with the theory that crushability and impaction are directly related. Impaction of an encapsulated toner with a high molecular weight polystyrene wall is approximately one half that of a similar core material encapsulated with a low molecular weight polystyrene.

Encapsulation of a plasticized soft solid adhesive in a shell material having desirable electrostatographic properties provides an electrostatographic toner which has good mechanical and electrical properties and which can be fixed on paper or other suitable transfer medium by unheated pressure rolls at low pressures. The core materials are selected to provide a strong adhesive bond between the image substrate and the shell material under the conditions employed to rupture the capsules. The shell material, capsule geometry, and the shell to core ratio are selected to provide the desired electrostatographic and machine performance properties and yet permit the capsules to be ruptured at low roll pressures.

It has been found that microcapsules containing plasticized adhesive soft solid cores encased in a shell material such as a copolymer of styrene and a lower alkyl methacrylate or a shell material such as a polystyrene can be employed as an electrostatographic toner which can be fixed to a substrate by passage through unheated steel pressure rolls. The fixed images exhibit no tendency to smear and are nontacky under normal conditions of usage. In addition, it has been found that the addition of a plasticizer to the polymeric core materials of the encapsulated toners of this invention lowers the Tg of the core materials thus improving the fixability of the toners.

Any suitable adhesive, soft solid material may be employed as the plasticized polymeric core material for the encapsulated pressure fixable toners of this invention. Typical core materials include polyesters (e.g., Epon 872, available from Shell Chemical Company), polyester based urethane polymers (e.g., Formrez P-211, P-410, P-610 available from Witco Chemical Corporation), epoxidized phenolformaldehyde resin (e.g., Epoxy-Novolak ERLB-0449, available from Union Carbide Corporation), polyisobutylene (e.g., Oppanol B-10, available from Badische Anilin and Soda Fabrik, West Germany), polyamides such as the reaction product of dimerized linoleic acid with diamines or polyamines (e.g., Versamid 100, Versamid 712, Versamid 948, and Versamid 950 available from General Mills Chemical Division) and the reaction products of dimer acids with linear diamines (e.g., Emerez 1530, available from Emery Industries, Incorporated), 50/**50** or 45/**55** docosyl acrylate/styrene copolymers, materials which exhibit shear thinning viscosity behavior due to intermolecular hydrogen bonding such as carboxyl terminated substances prepared by the reaction of anhydrides and hydroxyl compounds, for example, the trimellitate ester of dihydroxyl terminated polycaprolactone, polyurethane elastomers (e.g., Estane 5701, **5702, 5710** and 5714 available from B. F. Goodrich Company), polyester based alkyl resins, ester gums such as rosin esters and modified rosin esters, polyvinylacetate, the polymeric reaction product of isopropylidenediphenoxypropanol and adipic acid, the polymeric reaction porduct of isopropylidenediphenoxypropanol and sebacic acid, C_{36} di-urea and mixtures thereof.

Any suitable material may be employed as the polymeric shell material for the encapsulated pressure fixable plasticized toners of this invention. The shell material may be a homopolymer or a copolymer of two or more monomers. Typical shell materials include: polystyrenes (e.g., PS-2, Styron 666 and Styron 678 available from Dow Chemical Company; Lustrex 99, available from Monsanto Chemical Company); polymonochlorostyrene; copolymers such as styrene-methacrylates and styrene-acrylates; polycarbonates (e.g., Lexan 101, a poly-(4,4'-dioxydiphenyl-2,2'-propane carbonate available from General Electric Company); polyethers; low molecular weight polyethylenes; polymeric acrylic and methacrylic esters, fumarate polyester resins (e.g., Atlac Bisphenol A, available from Atlas Chemical Company), Dion-Iso polyester resins available from Diamond Shamrock Chemical Company, Krumbhaar polyester resins (e.g., K-2200 and K-1979, available from Lawter Chemicals, Incorporated); polyamides such as the reaction product from terephthalic acid and alkyl substituted hexamethylene diamine (e.g., Trogamid T, available from Dynamit Nobel Sales Corporation), the reaction products of dimerized linoleic acid with diamines or polyamines (e.g., Versamid 712, 948 and 950, available from General Mills Chemical Division), the reaction products of dimer acids with linear diamines (e.g., Emerez 1538, **1540** and 1580 available from Emery Industries, Incorporated); naturally occurring materials such as gelatin, zein, gum arabic and the like; and mixtures thereof.

In the preparation of the encapsulated electrostatographic plasticized toner materials of this invention, although any one of many known resinous developing materials which are electroscopic in nature and which form coherent spheres when they come out of solution may be used to form the shell materials solution, it has generally been found that electrically insulating, water insoluble synthetic polymer resins form toners having

many highly desirable properties, especially for use in automatic copying machines. Thus, the shell material is generally selected to provide desirable electrostatographic properties such as resistance to toner blocking, resistance to agglomeration, resistance to impaction onto carrier particles, proper triboelectrification, crushability, and fixability. Unlike the polymeric resins used in conventional toners such as those designed for heat fusing, the shell materials for the pressure fixable toners of this invention need not necessarily be thermoplastic. In the preparation of the electrostatographic encapsulated toners of this invention, shell material resins containing a relatively high percentage of a styrene resin are preferred because they provide good image quality. The styrene resin may be a homopolymer of styrene or styrene homologues or copolymers of styrene with other monomers containing a single methylene group attached to a carbon atom by a double bond. Thus, typical monomeric materials which may be copolymerized with styrene by addition polymerization include: p-chlorostyrene; vinyl naphthalene; ethenically unsaturated mono-olefins such as ethylene, propylene, butylene, isobutylene and the like; vinyl esters such as vinyl acetate, vinyl propionate, vinyl benzoate, vinyl butyrate and the like; esters of alpha-methylene aliphatic monocarboxylic acids such as methyl acrylate, ethyl acrylate, isobutyl acrylate, dodecyl acrylate, n-octyl acrylate, 2-chloroethyl acrylate, phenyl acrylate, methyl-alpha-chloroacrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylate, isopropyl methacrylate, butyl methacrylate and the like; acrylonitrile methacrylonitrile; acrylamide, vinyl ethers such as vinyl methyl ether, vinyl isobutyl ether, vinyl ethyl ether, and the like; vinyl ketones such as vinyl methyl ketone, vinyl hexyl ketone, methyl isopropenyl ketone and the like; vinylidene halides such as vinylidene chloride, vinylidene chlorofluoride and the like; and N-vinyl compounds such as N-vinyl pyrrole, N-vinyl carbazole, N-vinyl indole, N-vinyl pyrrolidene and the like; and mixtures thereof. The styrene resins may also be formed by the polymerization of mixtures of two or more of these unsaturated monomeric materials with a styrene monomer.

For the encapsulated electrostatographic plasticized toner materials of this invention, the shell material of the encapsulated toner should have a blocking temperature of at least about 100°F. When the encapsulated toner is characterized by a blocking temperature less than about 100°F., the toner particles may tend to agglomerate during storage and machine operation and also form undesirable films on the surface of reusable photoreceptors which adversely affect image quality. It is to be understood that the specific formulas given for units contained in the shell material resins of this invention represent the vast majority of the units present, but do not exclude the presence of monomeric units or reactants other than those which have been shown.

The ratio of shell material to core material may be any suitable value and generally is varied with the thickness, strength, porosity, and solubility characteristics of the shell desired. Thus, generally, the ratio of shell material to core material may be between about 99 parts by weight of shell material to about 1 part by weight of core material and about 1 part by weight of shell material to about 99 parts by weight of core material. However, the preferred range is between a ratio of about 7 parts by weight of shell material to about 1 part by weight of core material and about 1 part by weight of shell material to about 7 parts by weight of core material as encapsulated toner particles having the best surface characteristics are obtained. In general, the thickness of the shell material may be controlled by the ratio of the amount of core material to be encapsulated to the amount of shell material. Thus, if a thicker shell layer is desired, more shell material should be used since the ratio of shell to core material generally remains constant during the preparation of the encapsulated toner particles of this invention. In addition, the size of the encapsulated particle also generally affects the shell thickness since the smaller the particle, the smaller the shell thickness at a constant core to shell ratio.

Any suitable material may be employed as the plasticizer for the core material of the encapsulated toners of this invention. Typical plasticizers for the core materials of the encapsulated toners of this invention include low molecular weight polyesters such as Santicizer 405, Santicizer 409, and Santicizer 411 available from Monsanto Chemical Company; polychlorinated polyphenyls such as the Aroclor series available from Monsanto Chemical Company; esters of phosphoric acid such as tricresyl phosphate and triphenyl phosphate; stearate and benzoate esters of polyhydroxy compounds such as pentaerythritol; sulfonamides such as n-ethyl, n-cyclohexyl, unsubstituted sulfonamides such as toluene sulfonamide; phthalates such as diethyl, dibutyl, dioctyl, and diphenyl; alkoxylated bisphenol compounds such as isopropylidenediphenoxypropanol; and mixtures thereof. The low molecular weight polyesters are preferred as the plasticizers for the core materials of the encapsulated toners of this invention because of their plasticizing capability with regard to the core materials and because of their incompatibility with shell materials such as polystyrene.

The ratio of plasticizer to polymeric core material may be any suitable value and generally is varied with the fixing mode employed and the fixing properties desired. Thus, generally, satisfactory results are obtained when the ratio of plasticizer to polymeric core material is between about 1 part by weight of plasticizer material to about 99 parts by weight of polymeric core material and about 50 parts by weight of plasticizer material to about 50 parts by weight of polymeric core material. However, the preferred range is between a ratio of about 5 parts by weight of plasticizer material to about 95 parts by weight of polymeric core material and about 30 parts by weight of plasticizer material to about 70 parts by weight of polymeric core material as encapsulated toner particles having the best surface characteristics and fixing properties are obtained. For optimum results, the ratio of plasticizer to polymeric core material is between about 10 parts by weight of plasticizer material to about 90 parts by weight of polymeric core material and about 30 parts by weight of plasticizer material to about 70 parts by weight of polymeric core material.

The core, shell, or both the core and shell materials of the encapsulated toners of this invention may be pigmented or dyed, or pigmented and dyed by the addition of suitable pigment or dye or both pigment and dye to the core and shell materials. The pigment or dye, or pigment and dye, in many cases can be concentrated in the core or in the shell material or at the interface between the core and shell material. Thus, a dye may be

concentrated in the phase, core or wall, in which it is soluble. In some cases, dyes will form separate phases like pigment particles because of insufficient solubility in the core and wall materials. Thus, the encapsulated toners of the present invention include a colorant, either a pigment or dye, in a quantity sufficient to impart color to the resin composition, generally in a quantity up to about 25%, by weight, and particularly from about 1% to about 20%, by weight, of the toner, whereby the resulting toner will form a clearly visible image on a transfer member.

Any suitable pigment or dye or pigment and dye may be employed as the colorant for the encapsulated electrostatographic plasticized toner particles of this invention. Electrostatographic toner colorants are well known and include, for example, carbon black, nigrosine dye, aniline blue, Calco Oil Blue, chrome yellow, chrome green, ultramarine blue, cobalt blue, duPont Oil Red, benzidine yellow, Quinoline Yellow, methylene blue chloride, phthalocyanine blue or green, Malachite Green Oxalate, lamp black, Rose Bengal, and mixtures thereof. The pigment or dye, or pigment and dye, 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 electrostatographic copies of typed documents are desired, the toner may comprise a black pigment such as carbon black or a black dye such as Amaplast Black dye, available from National Aniline Products, Incorporated. Preferably, the pigment is employed in an amount from about 3 percent to about 20 percent by weight based on the total weight of the colored toner because better images are obtained. If the toner colorant employed is a dye, substantially smaller quantities of colorant may be used.

When a pigment is employed as a colorant for the encapsulated electrostatographic plasticized toner particles of this invention, the method of preparation thereof may comprise in dispersing an insoluble pigment by severe agitation in a solution of the desired core and shell materials followed by drying under controlled conditions so that part of the solvent is driven off and the core material separates forming finely divided particles and further removal of the solvent causes the shell material to phase separate around the core material thus forming the wall. Substantially no free pigment is produced by this process since the pigment may be found in the core or wall material or at the interface between the core and wall material.

Obviously, the pigment need not necessarily be included in both the core and the wall of the encapsulated toner particle, but instead, may be included in only one of these. Since high concentrations of pigment may adversely affect the viscous flow characteristics of some core materials, it is usually desirable that the pigment concentration be low if the pigment is to be concentrated in the core. Likewise, if the pigment is to form part of the shell, the pigment concentration is preferably not so high as to inhibit the formation of an impermeable shell or otherwise adversely affect the integrity of the shell. Since the encapsulated toner particles will generally be produced in sizes ranging from about 0.5 to about 35 microns, the pigment should preferably have a diameter of less than about 0.1 micron and wherever possible should be smaller as this contributes to the uniformity of end product coloration. In any event, the diameter of the pigment particle or other insoluble material should be less than about 75 percent by volume of the average core diameter.

Any suitable pressure may be employed to fix the toners of this invention. Typical pressures are those below about 600 pli since higher pressures tend to calander some paper substrates and change their texture and finish. In any event, the upper limit of usable pressure is a function of the substrate used. Any suitable temperature may be employed to fix the toners of this invention with a heat assisted pressure fixing electrostatographic device. Typical temperatures in such a device include temperatures from about 100°F. to about 160°F.

Any suitable encapsulation manufacturing process may be employed to produce the encapsulated plasticized toner materials of this invention. Typical encapsulation techniques are disclosed in "Microencapsulation Technology," 1969, by Dr. M. W. Ranney, Noyes Development Corporation, Park Ridge, N.J. In the preferred method of preparing the toners of this invention, the substantially soluble portion of a core material and a plasticizer material may be encapsulated in the substantially soluble portion of a shell material having a solubility different from the core material and plasticizer material by dissolving the core material, the plasticizer material, and the shell material in at least one relatively volatile solvent to form a solution, and substantially simultaneously forming small individual droplets of the solution, removing at least a portion of the solvent from each individual droplet by evaporation thereby increasing the concentration of the dissolved core material, the plasticizer material, and the shell material whereby substantially all of the core material and plasticizer material preferentially phase separate as a solvent poor phase, and removing additional solvent from each droplet whereby the shell material deposits around the core material and plasticizer material to form substantially dry, small spherical particles comprising the core material and plasticizer material encapsulated with the shell material.

Basically, the above technique for the preparation of the toner materials of this invention comprises selection of the ingredients, including the solvent or mixture of solvents, so that the change in concentration of solvent or solvents and dissolved or dispersed materials during drying and in some cases, the change in pH or temperature of the solution, will cause the core material and plasticizer material to phase separate as a solvent poor, high surface tension phase in a solution of shell material. The solution of shell material will thereafter surround and encapsulate the core phase and ultimately form a substantially dry solid capsule shell upon evaporation of the solvent. The separated core material phase and the separated shell material phase may be solvent poor phases and not solvent free phases. The thus produced encapsulated product can be collected in dry, free flowing form by any conventional or suitable means.

It is understood that although specific methods of preparing the encapsulated toner particles of this invention have been disclosed herein, other methods such as disclosed in U.S. Pat. No. 3,338,991 to Insalaco, et al., U.S. Pat. No. 3,326,848 to Clemens, et al, and U.S. Pat. No. 3,502,582 to Clemens, et al., may be employed.

Spray drying is the preferred unit operation capable of producing the encapsulated electrostatographic toner particles of this invention. Thus, the encapsulated electrostatographic plasticized toner particles of this invention may be prepared in the average particle size range of about 0.5 to about 1,000 microns. When the encapsulated electrostatographic toner particles of this invention are to be employed in cascade development processes, the toner should have an average particle diameter less than about 30 microns and preferably between about 3 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 nonmagnetic, 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 an electrostatic image is desired, the carrier particle is selected so 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 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 mixed are such that the electroscopic 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 do the carrier particles. Typical carriers include sodium chloride, ammonium chloride, aluminum potassium chloride, Rochelle salt, sodium nitrate, aluminum nitrate, potassium chlorate, granular zircon, granular silicon, methyl methacrylate, glass, steel, nickel, iron, ferrites, ferromagnetic materials, 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. No. 2,618,551; L. E. Walkup, et al., in U.S. Pat. No. 2,638,416; E. N. Wise in U.S. Pat. No. 2,618,552; R. J. Hagenbach, et al., in U.S. Pat. No. 3,591,503 and No. 3,533,835 ; and B. J. Jacknow, et al., in U.S. Pat. No. 3,526,533. 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 adherence 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. No. 3,186,838. Also, print deletion occurs when carrier beads adhere to electrostatographic imaging surfaces.

The toner compositions of the instant invention may be employed to develop electrostatic latent images on any suitable electrostatic latent image bearing surface including conventional photoconductive surfaces. Well known photoconductive materials include vitreous selenium, organic or inorganic photoconductors embedded in a nonphotoconductive 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. No. 2,803,542 to Ullrich, U.S. Pat. No. 2,970,906 to Bixby, U.S. Pat. No. 3,121,006 to Middleton, U.S. Pat. No. 3,121,007 to Middleton, and U.S. Pat. No. 3,151,982 to Corrsin.

The toners herein described are employed in a developer composition by loosely coating the toners on a suitable electrostatographic developer carrier surface to which the toners are affixed by electrostatic attraction as generally known in the art. Thus, for example, the toner compositions may be employed in the cascade development technique, as more fully described in U.S. Pat. No. 2,618,551 to Walkup, U.S. Pat. No. 2,618,552 to Wise, and U.S. Pat. No. 2,638,416 to Walkup, et al. In the cascade development technique, the developer composition is produced by mixing toner particles with a carrier which may be either electrically conducting or insulating, magnetic or nonmagnetic, provided that the carrier material when brought in close contact with the toner particles acquires a charge having an opposite polarity to that of the toner whereby the toner adheres to and surrounds the carrier. Thus, the carrier material is selected in accordance with its triboelectric properties so that the toner is either above or below the carrier material in the triboelectric series, to provide a positively or negatively charged toner.

The herein described encapsulated plasticized toners may also include other materials generally employed for modifying the characteristics of a toner, such as conductive materials to modify the triboelectric properties thereof, and the use of such materials is deemed to be within the scope of those skilled in the art from the teachings herein.

The degree of contrast or other photographic qualities in the finished image may be varied by changing the relative proportions of toner and carrier material and the choice of optimum proportions is deemed to be within the scope of those skilled in the art. In general, however, the toners of this invention are employed in amounts to provide weight ratios of carrier to toner of from about 10:1 to about 250:1, preferably from about 30:1 to about 100:1 with carrier particles of the size described above to produce a dense readily transferable image.

In addition to the use of particles to provide the carrier surface, the bristles of a fur brush may also be used. Here also, the toner particles acquire an electrostatic charge of polarity determined by the relative position of the toner particles and the fur fibers in the triboelectric series. The toner particles form a coating on the bristles of the fur clinging thereto by reason of the electrostatic attraction between the toner and the fur just as the toner clings to the surface of the carrier particles. The general process of fur brush development is de-

scribed in greater detail in U.S. Pat. No. 3,251,706 to L. E. Walkup.

Even more closely related to the cascade carrier development is magnetic brush development. In this process, a carrier is selected having ferromagnetic properties and selected relative to the toner in a triboelectric series so as to impart the desired electrostatic polarity to the toner and carrier as in cascade carrier development. On inserting a magnet into such a mixture of toner and magnetic material, the carrier particles align themselves along the lines of force of the magnet to assume a brushlike array. The toner particles are electrostatically coated on the surface of the carrier particles. Development proceeds as in regular cascade carrier development on moving the magnet over the surface bearing the electrostatic image so that the "bristles" of the magnetic brush contact the electrostatic image bearing surface.

Still another method of carrier development is known as sheet carrier development in which the toner particles are placed on a sheet of paper, plastic, or metal. This process is described in U.S. Pat. No. 2,895,847 to C. R. Mayo. As described therein, the electrostatic attraction between the sheet surface and toner particles necessary to assure electrostatic attraction therebetween may be obtained by leading the sheet through a mass of electroscopic toner particles whereby there is obtained a rubbing or sliding contact between the sheet and the toner. In general, it is desirable to spray the surface of the sheet bearing the electroscopic toner particles with ions of the desired polarity as by the use of a corona charging device as described in the patent of Mayo. The resulting image of toner particles on the image bearing surface may then be transferred to a suitable transfer member to form the final copy. The transfer of the toner particles may be effected adhesively or electrostatically as known in the art.

The toner, as should be apparent from the hereinabove teachings, may be employed in a wide variety of developer compositions by electrostatically coating the toner composition to a suitable carrier surface, which is subsequently passed over a latent image bearing surface. The toners of the invention may also be employed for developing an electrostatic latent image formed by other than electrostatographic means; for example, the development of electrostatic latent images formed by pulsing electrodes as employed in electrostatic printing processes. In addition, the toners of the invention may be employed for developing an electrostatic latent image on a surface other than a photoconductive insulating surface. Therefore, the overall invention is not limited to a specific technique for forming or developing an electrostatic latent image or to a specific carrier for the toner.

The toners of the present invention are capable of being fixed to a suitable support medium such as paper to provide a finished copy by the application of pressure; in some cases, the pressure fixing is heat assisted, but in such cases, the amount of heat required is significantly less than that required in prior art heat fixing systems. The pressure required for effecting such pressure fixing varies with the particular toner employed. The pressure is preferably provided by pressing the transfer material having the toner image thereon between a pair of polished metal rollers that are in contact with each other under a specified pressure. It is to be understood, however, that although the toners of the present invention are particularly suitable for the preparation of a final copy by pressure fixing, such toners may also be fixed by conventional procedures; e.g., heat fusing.

A pressure fixable toner which can be fixed at low pressures to provide a fixed image comparable to those that have been fixed by heating substantially reduces fixing energy requirements, eliminates warmup time for the fixing apparatus, and also the possibility of fires caused by paper transport failures. Prior art pressure fixable toners fail to achieve these advantages because they require excessive pressures, as in the case of toners which are not encapsulated, or tend to smear because of the unfixed, broken capsule shells in the case of encapsulated liquids. The use of a plasticized adhesive core coupled with provision for adjustment of the electrostatographic properties of the shell permits attaining the desired fixing properties of the toner material without smearing of the ruptured shells by bonding the cores and shells tightly to the paper. The diffusion of a liquid core material through the capsule shell, even though too slight to cause a serious loss of core material in storage, can cause variable electrostatographic properties. Another advantage of the encapsulated soft solids of this invention over encapsulated liquids is that the molecular size and physical properties of these soft solids prevent diffusion of the core material through the shell.

DESCRIPTION OF PREFERRED EMBODIMENTS

This invention is further illustrated by the following examples but it is to be understood that the scope of the invention is not to be limited thereby. Unless otherwise specified, all parts are by weight.

In the following examples, the term "stick point" means the temperature at which a material adheres to a metallic substrate; for example, a continuous line of sample is equilibrated on a Kofler Hot Bench for about 2 hours and then gently brushed away. The "stick point" is the lowest temperature at which the sample "sticks" to the metallic plate of the hot bench. Likewise, the term "blocking tests" refers to tests usually conducted on small open dishes of toner material at specific temperature conditions. The blocking temperature is determined as the lowest temperature to which the toner has been subjected for a period of equilibration and the "crusty" mass produced can no longer be easily broken down to the original particles. Also, the term "geometric standard deviation" is the deviation encountered in a particle size analysis, approximately measured as the ratio of the particle diameter which is greater than that of 84% of the sample to the particle diameter which is greater than that of 50% of the sample. In addition, the term "Taber Cycles" is the degree of fix obtained using a test method based on the resistance of a fixed toner image to abrasion with a Taber Abrader. A standard test pattern is printed at conditions to provide an integrated optical density as determined by a Welch Densitometer (Model 3834) of 1.2 $\pm$ 0.1. The test pattern is pressure fixed and then abraded with a weight of 375 grams on the abrader arm until the measured density is 80 percent of the initial density. The result is given as the number of "Taber Cycles" required to reduce the initial density by 20 percent.

EXAMPLE I

An encapsulated control toner material is prepared

from a solution comprising about 100.0 pounds of a polystyrene (PS-2) and about 100.0 pounds of the reaction product of isopropylidenediphenoxypropanol and adipic acid having a number average molecular weight of 2900 in a mixture of chloroform and heptane at a 2:3 chloroform:heptane volume ratio. A carbon black is dispersed in the solution by severe agitation. The final concentrations are about 4.8% polystyrene, about 4.8% reaction product of isopropylidenediphenoxypropanol and adipic acid, about 0.4% carbon black, and about 90.0% solvent. The solution, with dispersed carbon black is spray dried usisng a Bown Engineering, Incorporated, laboratory model 50 inch diameter spray dryer with a spinning disk atomizer operating at about 21,000 r.p.m. and a feed rate of about 1.4 liters/minute. Drying air inlet temperature is about 155°F. and outlet air temperature is about 120°F. The dry product is a powder of about 14.0 micron diameter volume average particle size with a geometric standard deviation of about 1.70. Electron microscope examination shows the individual particles to be primarily spherical and have a pigmented core surrounded by a substantially clear shell. Stick point, blocking tests and examination of crushed particles with the scanning electron microscope all indicate that the shell is principally polystyrene and the core principally the reaction product of isopropylidenediphenoxypropanol and adipic acid, and carbon black. About 1 part by weight of the encapsulated toner particles were mixed with about 99 parts by weight of 250 micron glass carrier beads. Prints were made to provide an integrated optical denisty of 1.2 ± 0.1 in a modified Xerox 660 Copier having the fuser removed. Pressure fixing was performed in an apparatus having two steel rolls of about 3 inches each in diameter in contact with each other. The contact pressure between the two rolls may be varied as desired up to approximately 500 pli. The upper steel roll may be heated externally with a 2000 watt quartz infra-red lamp. The fuser temperature is regulated with a proportional temperature controller and is monitored by means of a thermistor in sliding contact with the center of the upper fuser roll. The prints made were pressure fixed at 400 pli without the assistance of heat. The degree of fix obtained is found to be about 3 Tabor Cycles.

EXAMPLE II

An encapsulated plasticized toner material is prepared from a solution comprising about 200.0 grams of a polystyrene (PS-2) and about 180.0 grams of the reaction product of isopropylidenediphenoxypropanol and adipic acid having a number average molecular weight of 2900 and about 20.0 grams of a low molecular weight polyester (Santicizer 411) as a plasticizer for the reaction product of isopropylidenediphenoxypropanol and adipic acid in a mixture of chloroform and cyclohexane at a 1:2 chloroform:cyclohexane volume ratio. A carbon black is dispersed in the solution by severe agitation. The final concentrations are about 4.7% polystyrene, about 4.3% reaction product of isopropylidenediphenoxypropanol and adipic acid, about 0.5% polyester, about 0.5% carbon black, and about 90.0% solvent. The solution, with dispersed carbon black is spray dried using a Bowen Engineering, Incorporated, laboratory model 30 inch diameter spray dryer with a spinning disk atomizer operating at about 50,000 r.p.m. and a feed rate of about 200 ml/minute. Drying air inlet temperature is about 166°F. and outlet air temperature is about 130°F. The dry product is a powder of about 14.0 micron diameter volume average particle size with a geometric standard deviation of about 1.70. Electron microscope examination shows the individual particles to be primarily spherical and have a pigmented core surrounded by a substantially clear shell. Stick point, blocking tests and examination of crushed particles with the scanning electron microscope all indicate that the shell is principally polystyrene and the core principally the reaction product of isopropylidenediphenoxypropanol and adipic acid, polyester and carbon black. About 1 part by weight of the encapsulated plasticized toner particles were mixed with about 99 parts by weight of 250 micron glass carrier beads and substituted for the developer in the testing machine described in Example I. Under substantially identical test conditions, the degree of fix obtained is found to be about 6.0 Taber Cycles at 400 pli of pressure, and about 8.9 Taber Cycles at 500 pli of pressure. From these results, it is seen that the incorporation of the plasticizer for the core material substantially increases the degree of fix obtained over that with the toner composition of Example I. In addition, no image smearing was observed. Upon further examination, it was found that the Tg of the reaction product of isopropylidenediphenoxypropanol and adipic acid is lowered from about 18°C. to about 6°C. Further, it was found that this plasticizer is substantially incompatible with the polystyrene and compatible with the reaction product of isopropylidenediphenoxypropanol and acipic adid which is a necessary property when preparing this toner composition by spray drying.

EXAMPLE III

An encapsulated plasticized toner material is prepared from a solution comprising about 323.0 grams of a polystyrene (PS-2) and about 258.4 grams of the reaction product of isopropylidenediphenoxypropanol and adipic acid having a number average molecular weight of 2900 and about 64.6 grams of a low molecular weight polyester (Santicizer 405) as a plasticizer for the reaction product of isopropylidenediphenoxypropanol and adipic acid in a mixture of chloroform and cyclohexane at 1:2 chloroform:cyclohexane volume ration. A carbon black is dispersed in the solution by severe agitation. The final concentrations are about 2.0% polystyrene, about 1.6% reaction product of isopropylidenediphenoxypropanol and adipic acid, about 0.4% polyester, about 0.2% carbon black, and about 95.8% solvent. The solution, with dispersed carbon black is spray dried using a Bowen Engineering, Incorporated, laboratory model 30 inch diameter spray dryer with a spinning disk atomizer operating at about 25,000 r.p.m. and a feed rate of about 200 ml/minute. Drying air inlet temperature is about 145°F. and outlet air temperature is about 121°F. The dry product is a powder of about 16.5 micron diameter volume average particle size with a geometric standard deviation of about 1.76. Electron microscope examination shows the individual particles to be primarily spherical and have a pigmented core surrounded by a substantially clear shell. Stick point, blocking tests and examination of crushed particles with the scanning electron microscope all indicate that the shell is principally polystyrene and the core principally the reaction product of isopropylidendiphenoxypropanol and adipic acid, poly-

ester and carbon black. About 1 part by weight of the encapsulated plasticized toner particles were mixed with about 99 parts by weight of 250 micron glass carrier beads and substituted for the developer in the testing machine described in Example I. Under substantially identical test conditions the degree of fix obtained is found to be about 22.3 Taber Cycles at 200 pli of pressure, about 57.8 Taber Cycles at 400 pli of pressure, and about 97.8 Taber Cycles at 500 pli of pressure. From these results, it is seen that the incorporation of the plasticizer for the core material substantially increases the degree of fix obtained over that with the toner composition of Example I. In addition, no image smearing was observed. Upon further examination, it was found that the Tg of the reaction product of isopropylidenediphenoxypropanol and adipic acid is lowered from about 18°C. to about −11°C. As in Example II, it was found that this plasticizer is substantially incompatible with the polystyrene and compatible with the reaction product of isopropylidenediphenoxypropanol and adipic acid.

EXAMPLE IV

An encapsulated plasticized toner material is prepared from a solution comprising about 200.0 grams of the reaction product of a dimer acid and a linear diamine (Emerez 1540) and about 190.0 grams of the reaction product of isopropylidenediphenoxypropanol and adipic acid having a number average molecular weight of 2,900 and about 10.0 grams of a low molecular weight polyester (Santicizer 409) as a plasticizer for the reaction product of isopropylidenediphenoxypropanol and adipic acid in a mixture of chloroform and isopropanol at a 1:2 chloroform:isopropanol volume ratio. A carbon black is dispersed in the solution by severe agitation. The final concentrations are about 4.75% reaction product of dimer acid and linear diamine, about 4.5% reaction product of isopropylidenediphenoxypropanol and adipic acid, about 0;.25% polyester, about 0.5% carbon black, and about 90.0% solvent. The solution, with dispersed carbon black is spray dried using a Bowen Engineering, Incorporated, laboratory model 30 inch diameter spray dryer with a spinning disk atomizer operating at about 50,000 r.p.m. and a feed rate of about 200 ml/minute. Drying air inlet temperature is about 151°F. and outlet air temperature is about 118°F. The dry product is a powder of about 15.8 micron diameter volume average particle size with a geometric standard deviation of about 1.70. Electron microscope examination shows the individual particles to be primarily spherical and have a pigmented core surrounded by a substantially clear shell. Stick point, blocking tests and examination of crushed particles with the scanning electron microscope all indicate that the shell is principally the reaction product of dimer acid and linear diamine and the core principally the reaction product of isopropylidenediphenoxypropanol and adipic acid, polyester and carbon black. About 1 part by weight of the encapsulated plasticized toner particles were mixed with about 99 parts by weight of 250 micron glass carrier beads and substituted for the developer in the testing machine described in Example I. Under substantially identical test conditions the degree of fix obtained is found to be about 4.3 Taber Cycles at 400 pli of pressure, and about 5.2 Taber Cycles at 500 pli of pressure. From these results, it is seen that this composition provides a degree of fix substantially greater than that obtained with the toner composition of Example I. In addition, no image smearing was observed. Further, it was found that this plasticizer is substantially incompatible with the reaction product of a dimer acid and a linear diamine employed as the shell material.

EXAMPLE V

An encapsulated plasticized toner material is prepared from a solution comprising about 323.0 grams of a polystyrene (PS-2) and about 306.8 grams of the reaction product of isopropylidenediphenoxypropanol and adipic acid having a number average molecular weight of 2900 and about 16.2 grams of a low molecular weight polyester (Santicizer 405) as a plasticizer for the reaction product of isopropylidenediphenoxypropanol and adipic acid in a mixture of chloroform and cyclohexane at a 1:2 chloroform:cyclohexane volume ratio. A carbon black is dispersed in the solution by severe agitation. The final concentrations are about 2.0% polystyrene, about 1.6% reaction product of isopropylidenediphenoxypropanol and adipic acid, about 0.2% polyester, about 0.2% carbon black, and about 96.0% solvent. The solution, with dispersed carbon black is spray dried using a Bowen Engineering, Incorporated, laboratory model 30 inch diameter spray dryer with a spinning disk atomizer operating at about 50,000 r.p.m. and a feed rate of about 200 ml/minute. Drying air inlet temperature is about 150°F. and outlet air temperature is about 130°F. The dry product is a powder of about 14.5 micron diameter volume average particle size with a geometric standard deviation of about 1.72. Electron microscope examination shows the individual particles to be primarily spherical and have a pigmented core surrounded by a substantially clear shell. Stick point, blocking tests and examination of crushed particles with the scanning electron microscope all indicate that the shell is principally polystyrene and the core principally the reaction product of isopropylidenediphenoxypropanol and adipic acid, polyester and carbon black. About 1 part by weight of the encapsulated plasticized toner particles were mixed with about 99 parts by weight of 250 micron glass carrier beads and substituted for the developer in the testing machine described in Example I. Under substantially identical test conditions the degree of fix obtained is found to be about 7.1 Taber Cycles at 400 pli of pressure, and about 11.3 Taber Cycles at 500 pli of pressure. From these results, it is seen that the incorporation of the plasticizer for the core material substantially increases the degree of fix obtained over that with the toner composition of Example I. In addition, no image smearing was observed. Further, it was found that this plasticizer is substantially incompatible with the polystyrene and compatible with the reaction product of isopropylidenediphenoxypropanol and adipic acid.

EXAMPLE VI

An encapsulated plasticized toner material is prepared from a solution comprising about 323.0 grams of polystyrene (PS-2) and about 290.7 grams of the reaction product of isopropylidenediphenoxypropanol and adipic acid having a number average molecular weight of 2,900 and about 32.2 grams of a low molecular weight polyester (Santicizer 405) as a plasticizer for the reaction product of isopropylidenediphenoxypropanol and adipic acid in a mixture of chloroform

and cyclohexane at a 1:2 chloroform:cyclohexane volume ratio. A carbon black is dispersed in the solution by severe agitation. The final concentrations are about 2.0% polystyrene, about 1.6% reaction product of isopropylindenediphenoxypropanol and adipic acid, about 0.4% polyester, about 0.2% carbon black, and about 95.8% solvent. The solution, with dispersed carbon black is spray dried using a Bowen Engineering, Incorporated, laboratory model 30 inch diameter spray dryer with a spinning disk atomizer operating at about 25,000 r.p.m. and a feed rate of about 200 ml/minute. Drying air inlet temperature is about 145°F. and outlet air temperature is about 121°F. The dry product is a powder of about 14.5 micron diameter volume average particle size with a geometric standard deviation of about 1.74. Electron microscope examination shows the individual particles to be primarily spherical and have a pigmented core surrounded by a substantially clear shell. Stick point, blocking tests and examination of crushed particles with the scanning electron microscope all indicate that the shell is principally polystyrene and the core principally the reaction product of isopropylidenediphenoxypropanol and adipic acid, polyester and carbon black. About 1 part by weight of the encapsulated plasticized toner particles were mixed with about 99 parts by weight of 250 micron glass carrier beads and substituted for the developer in the testing machine described in Example I. Under substantially identical test conditions the degree of fix obtained is found to be about 22.4 Taber Cycles at 400 pli of pressure, and about 31.6 Taber Cycles at 500 pli of pressure. From these results, it is seen that the incorporation of the plasticizer for the core material substantially increases the degree of fix obtained over that with the toner composition of Example I. In addition, no image smearing was observed. Further, it was found that this plasticizer is substantially incompatible with the polystyrene and compatible with the reaction product of isopropylidenediphenoxypropanol and adipic acid.

EXAMPLE VII

An encapsulated plasticized toner material is prepared from a solution comprising about 200.0 grams of a polystyrene (PS-2) and about 190.0 grams of the reaction product of isopropylidenediphenoxypropanol and adipic acid having a number average molecular weight of 2900 and about 10.0 grams of a low molecular weight polyester (Santicizer 411) as a plasticizer for the reaction product of isopropylidenediphenoxypropanol and adipic acid in a mixture of chloroform and cyclohexane at a 1:2 chloroform:cyclohexane volume ratio. A carbon black is dispersed in the solution by severe agitation. The final concentrations are about 4.70% polystryene, about 4.75% reaction product of isopropylidendiphenoxypropanol and adipic acid, about 0.25% polyester, about 0.50% carbon black, and about 89.8% solvent. The solution, with dispersed carbon black is spray dried using a Bowen Engineering, Incorporated laboratory model 30 inch diameter spray dryer with a spinning disk atomizer operating at about 50,000 r.p.m. and a feed rate of about 200 ml/minute. Drying air inlet temperature is about 166°F. and outlet air temperature is about 130°F. The dry product is a powder of about 12.5 micron diameter volume average particle size with a geometric standard deviation of about 1.74. Electron microscope examination shows the individual particles to be primarily spherical and have a pigmented core surrounded by a substantially clear shell. Stick point, blocking tests and examination of crushed particles with the scanning electron microscope all indicate that the shell is principally polystyrene and the core principally the reaction product of isopropylidenediphenoxypropanol and adipic acid, polyester and carbon black. About 1 part by weight of the encapsulated plasticized toner particles were mixed with about 99 parts by weight of 250 micron glass carrier beads and substituted for the developer in the testing machine described in Example I. Under substantially identical test conditions, the degree of fix obtained is found to be about 4.6 Taber Cycles at 400 pli of pressure, and about 5.5 Taber Cycles at 500 pli of pressure. From these results, it is seen that the incorporation of the plasticizer for the core material substantially increases the degree of fix obtained over that with the toner composition of Example I. In addition, no image smearing was observed. Further, it was found that this plasticizer is substantially incompatible with the polystryene and compatible with the reaction product of isopropylidenediphenoxypropanol and adipic acid.

EXAMPLE VIII

An encapsulated plasticized toner material is prepared from a solution comprising about 200.0 grams of a polystyrene (PS-2) and about 160.0 grams of the reaction product of isopropylidenediphenoxypropanol and adipic acid having a number average molecular weight of 2900 and about 40.0 grams of a low molecular weight polyester (Santicizer 411) as a plasticizer for the reaction product of isopropylidenediphenoxypropanol and adipic acid in a mixture of chloroform and cyclohexane at a 1:2 chloroform:cyclohexane volume ratio. A carbon black is dispersed in the solution by severe agitation. The final concentrations are about 4.7% polystyrene, about 3.8% reaction product of isopropylidenediphenoxypropanol and adipic acid, about 1.0% polyester, about 0.5% carbon black, and about 90.0% solvent. The solution, with dispersed carbon black is spray dried using a Bowen Engineering, Incorporated, laboratory model 30 inch diameter spray dryer with a spinning disk atomizer operating at about 50,000 r.p.m. and a feed rate of about 200 ml/minute. Drying air inlet temperature is about 165°F. and outlet air temperature is about 130°F. The dry product is a powder of about 13.0 micron diameter volume average particle size with a geometric standard deviation of about 1.75. Electron microscope examination shows the individual particles to be primarily spherical and have a pigmented core surrounded by a substantially clear shell. Stick point, blocking tests and examination of crushed particles with the scanning electron microscope all indicate that the shell is principally polystyrene and the core principally the reaction product of isopropylidenediphenoxypropanol and adipic acid, polyester and carbon black. About 1 part by weight of the encapsulated plasticized toner particles were mixed with about 99 parts by weight of 250 micron glass carrier beads and substituted for the developer in the testing machine described in Example I. Under substantially identical test conditions the degree of fix obtained is found to be about 27.4 Taber Cycles at 400 pli of pressure, and about 36.3 Taber Cycles at 500 pli of pressure. From these results, it is seen that the incor-

poration of the plasticizer for the core material substantially increases the degree of fix obtained over that with the toner composition of Example I. In addition, no image smearing was observed. Further, it was found that this plasticizer is substantially incompatible with the polystyrene and compatible with the reaction product of isopropylidenediphenoxypropanol and adipic acid.

EXAMPLE IX

An encapsulated plasticized toner material is prepared from a solution comprising about 500.0 grams of a polystyrene (PS-2) and about 480.0 grams of the reaction product of isopropylidenediphenoxypropanol and adipic acid having a number average molecular weight of 2900 and about 120.0 grams of isopropylidenediphenoxypropanol as a plasticizer for the reaction product of isopropylidenediphenoxypropanol and adipic acid in a mixture of chloroform and heptane at a 1:1.3 chloroform:heptane volume ratio. A carbon black is dispersed in the solution by severe agitation. The final concentrations are about 4.5% polystyrene, about 4.3% reaction product of isopropylidenediphenoxypropanol and adipic acid, about 1.0% isopropylidenediphenoxypropanol, about 0.5% carbon black, and about 89.7 % solvent. The solution, with dispersed carbon black is spray dried using a Bowen Engineering, Incorporated laboratory model 30 inch diameter spray dryer with a spinning disk atomizer operating at about 50,000 r.p.m. and a feed rate of about 200 ml/minute. Drying air inlet temperature is about 163°F. and outlet air temperature is about 135°F. The dry product is a powder of about 11.5 micron diameter volume average particle size with a geometric standard deviation of about 1.71. Electron microscope examination shows the individual particles to be primarily spherical and have a pigmented core surrounded by a substantially clear shell. Stick point, blocking tests examination of crushed particles with the scanning electron microscope all indicate that the shell is principally polystyrene and the core principally the reaction product of isoproplidenediphenoxypropanol and adipic acid, isoproplidenediphenoxypropanol, and carbon black. About 1 part by weight of the encapsulated plasticized toner particles were mixed with about 99 parts by weight of 250 micron glass carrier beads and substituted for the developer in the testing machine described in Example I. Under substantially identical test conditions the degree of fix obtained is found to be about 5.3 Taber Cycles at 400 pli of pressure, and about 7.5 Taber Cycles at 500 pli of pressure. From these results, it is seen that the incorporation of the plasticizer for the core material substantially increases the degree of fix obtained over that with the toner composition of Example I. In addition, no image smearing was observed. Further, it was found that this plasticizer is substantially incompatible with the polystyrene and compatible with the reaction product of isopropylidenediphenoxy-propanol and adipic acid.

EXAMPLE X

An experiment was conducted to determine whether the flow properties of the toner material of Example IX could be improved. Poor toner flowability can become a major problem in toner packaging and toner dispensing. Thus, the flowability of the toner material of Example IX with various amounts of a powdered hydrophobic silica, Aerosil R-972, was studied relative to Xerox 364 toner. Flowability was measured by determining the amount of toner which would pass through a sieve under controlled conditions. The results obtained agree with the observed dispensing behavior in simulated machine testing. Thus, the silica was dispersed in the toner at concentrations from about 0.02% to about 2.0% by weight of the toner by tumbling the samples end over end in a can tumbler. The triboelectric values for the samples were measured versus homogeneous 450 micron glass carrier beads. The developers were roll-milled in 8 ounce glass jars for three hours, and triboelectric measurements were made at 10, 30 and 180 minutes. The data obtained indicated that less than 2.0% silica is sufficient to greatly increase the toner flowability and markedly effect the triboelectric characteristics of the toner. It was found that the addition of about 0.05% of silica provides a toner flowability comparable to Xerox 364 toner. The addition of between about 0.1% and 2.0% silica substantially improved the stability of the triboelectric properties of the toner material of Example IX with time and also provided an acceptable triboelectric value. There was also evidence that the addition of silica reduces triboelectric variations between different batches of the toner material of Example IX. The addition of the powdered silica noticeably improved the flowability of the toner material of Example IX in machine testing. The addition of silica also produced a high, stable triboelectricity.

EXAMPLE XI

The adhesive qualities of the core material of Example I was compared with that of the core material to which 2.0 percent by weight of plasticizer Santicizer 411 was added. This technique involves the use of a diluent, preferably a poor adhesive, instead of a solvent. Thus, an epoxy acrylate, Epocyrl U-12 available from Union Carbide Company, was used as the diluent. The peel adhesion test per ASTM-D903-49 was conducted as follows. About a 20.0 percent by weight solution of polymer in methyl ethyl ketone is cast onto aluminum plates to prepare about a 10 mil film. This film is dried to remove the solvent. The film is placed on a paper substrate and subjected to about 3300 p.s.i. pressure at room temperature. The film and paper substrate are then placed on the Instron and the force required to separate the film and the paper substrate is measured. The following comparative peel strengths were obtained.

Composition	Diluent %	Peel Strength (lb./in. of width)
Reaction product of isopropylidenediphenoxy-propanol and adipic acid	70	0.15
Reaction product of isopropylidenediphenoxy-propanol and adipic acid with plasticizer (2.0%)	70	0.92

From the above results, it can be seen that the addition of the plasticizer to the reaction product of isopropylidenediphenoxypropanol and adipic acid increases its peel strength by a factor of approximately 6 times under the above test conditions.

EXAMPLE XII

Melt viscosity determinations were taken on various blends of the reaction product of isopropylidenediphenoxypropanol and adipic acid with the plasticizers Santicizer 405 and Sancticizer 411. These measurements were made on the Brookfield LVT at 75°C., 100°C. and 125°C. using various shear rates. The room temperature viscosities (22°C.) were obtained by plotting a graph of log viscosity versus $1/(T\text{-}To) \times 10^2$. The 22°C. viscosities found by extrapolation are summarized in tabular form.

Composition	Plasticizer, %	Centipoise
1. Reaction product of isopropylidenediphenoxypropanol and adipic acid	none	8.7×10^{9}
2. Reaction product of isopropylidenediphenoxypropanol and adipic acid	Santicizer 411, 10.0	2.0×10^{8}
3. Reaction product of isopropylidenediphenoxypropanol and adipic acid	Santicizer 411, 20.0	3.5×10^{8}
4. Reaction product of isopropylidenediphenoxypropanol and adipic acid	Santicizer 411, 30.0	1.5×10^{7}
5. Reaction product of isopropylidenediphenoxypropanol and adipic acid	Santicizer 405, 20.0	7.9×10^{7}

From the above results, it is seen that there is a very definite decrease in the melt viscosity of the reaction product of isopropylidenediphenoxypropanol and adipic acid with the added plasticizers. In addition, the plasticizer Santicizer 405 has a greater effect than the plasticizer Santicizer 411.

EXAMPLE XIII

Glass transition temperature determinations were made on various blends of the reaction product of isopropylidenediphenoxypropanol and adipic acid with the low molecular polyesters Sancticizer 405, Santicizer 411, and the prepolymer isopropylidenediphenoxypropanol as plasticizers for the reaction product of isopropylidenediphenoxypropanol and adipic acid. The determinations were conducted on a Differential Thermal Analyzer available from the E. I. DuPont Company using either a 10° per minute or a 20° per minute heating rate. The glass transition temperature was taken at the intercept of the extrapolation of the baseline and the endotherm. Hot melt blends were prepared by melting the desired material in a common vessel and when quite fluid, stirring vigorously with a rotary mixer to ensure a good dispersion. The glass transition temperature measurements are summarized below in tabular form.

Composition	Plasticizer, %	Glass Transition Temperature, °C.
1. Reaction product of isopropylidenediphenoxypropanol and adipic acid	none	18
2. Polystyrene (PS-2)	none	69±1
3. Reaction product of isopropylidenediphenoxypropanol and adipic acid	Santicizer 405, 10	−0.2
4. Reaction product of isopropylidenediphenoxypropanol and adipic acid	Santicizer 405, 20	−11.0
5. Polystyrene (PS-2)	Santicizer 405, 10	63
6. Reaction product of isopropylidenediphenoxypropanol and adipic acid	Santicizer 411, 10	6
7. Polystyrene (PS-2)	Santicizer 411, 10	61
8. Reaction product of isopropylidenediphenoxypropanol and adipic acid	isopropylidenediphenoxypropanol, 20	8
9. Polystyrene (PS-2)	isopropylidenediphenoxypropanol, 10	57

From the above results, it is seen that the greatest plasticization, that is, lowering of the glass transition temperature, of the reaction product of isopropylidenediphenoxypropanol and adipic acid is obtained with Santicizer 405. Although not as great, Santicizer 411 likewise substantially plasticized the reaction product of isopropylidenediphenoxypropanol and adipic acid, with a lesser degree of plasticization being obtained with isopropylidenediphenoxypropanol. Further, it is seen that the glass transition temperatures obtained with blends of the polystyrene and the plasticizers indicate the plasticizers to be substantially incompatible with the polystyrene and lowered the glass transition temperature of the polystyrene only slightly in comparison to that of the reaction product of isopropylidenediphenoxypropanol and adipic acid.

The expression "developer composition" 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 intended merely as illustrations of the present invention. Various other suitable toner resins, additives, colorants and other components such as those listed above, may be substituted for those in the examples with similar results. Other materials may also be added to the toner composition to synthesize, 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. An electrostatographic toner material comprising finely divided toner particles, said toner particles having a particle size range from about 0.5 to about 1000 microns and a blocking temperature of at least about 100°F, said toner material comprising a colorant selected from the group consisting of pigments, dyes and mixtures thereof, an adhesive soft solid core material said core material including the reaction product of isopropylidenediphenoxypropanol and adipic acid and a plasticizer encapsulated in a shell material.

2. An electrostatographic developer material comprising a carrier and a toner comprising finely divided particles, having a particle size range from about 0.5 to about 1,000 microns and a blocking temperature of at

least about 100°F said toner material comprising a colorant selected from the group consisting of pigments, dyes and mixtures thereof, an adhesive soft solid core material, said core material including the reaction product of isopropylidenediphenoxypropanol and adipic acid and a plasticizer encapsulated in a shell material.

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