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IMAGING SYSTEMS

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ABSTRACT OF THE DISCLOSURE

Disclosed is a method of making spherical electrostatic toner particles comprising a colorant and a resin whereby they are prepared as a latex in the presence of at least one chain transfer agent. The resin is a vinyl polymer having a Tg value of from about 30° C. to about 85° C. and a weight average molecular weight between about 10,000 and 500,000. This toner may be employed in xerographic developers to develop electrostatic latent images.

BACKGROUND OF THE INVENTION

This invention relates in general to imaging systems, and more particularly, to improved xerographic developing materials, their manufacture and use. This application is a continuation-in-part of copending application Ser. No. 380,045, filed July 2, 1964, now U.S. Patent No. 3,326,848.

Xerography is perhaps best exemplified by the process of xerography as first described in U.S. Patent 2,297,691 to C. F. Carlson. In this process, a photoconductor is first given a uniform electrostatic charge over its surface and is then exposed to an image of activating electromagnetic radiation which selectively dissipates the charge in illuminated areas of the photoconductor while charge in the non-illuminated areas is retained thereby forming a latent electrostatic image. This latent electrostatic image is then developed or made visible by the deposition of finely divided, electroscopic marking mateiral, referred to in the art as toner on the surface of the photoconductor, which marking material conforms to the pattern of the latent electrostatic image. The visible image may then be utilized in a number of diverse ways. For example, the image may be viewed in situ on the photoconductive insulator, fixed in place on the photoconductive insulator or transferred to a second surface such as a sheet of paper and fixed in place thereon as desired depending upon whether the photoconductive insulating material is reusable as is the case with amorphous selenium photoconductive insulators or non-reusable as is the case with particulate zinc oxide-binder film type xerographic plates.

Although the original Carlson patent describes developing the latent electrostatic image by dusting it with various powders such as lycopodium, gum copal, cumarone-indene resin, various powdered dyes and the like, many other developing materials and techniques have been devised since that time. Some of the development techniques include brush development as described in U.S. Patent 3,015,305 to Hall, powder cloud development as described in U.S. Patent 2,918,900 to Carlson, liquid spray development as described in U.S. Patent 2,551,582 to Carlson, immersion development as described in U.S. Patent 3,010,842 to Ricker, loop development as described in U.S. Patent 2,761,416 to Carlson and donor development as described in U.S. Patent 2,895,847 to Mayo. However, it is more than likely that the commercial xerographic development technique most widely used today is the technique known as cascade development which is described in U.S. Patent 2,618,552 to Wise. This

development technique is carried out by rolling or cascading across the latent electrostatic image bearing surface, a developing mixture composed of relatively large carrier particles, each having a multiplicity of electrostatically adhering fine marking particles, known as toner particles on its surface. As this mixture cascades or rolls across the image bearing surface, the toner particles are electrostatically deposited on the charged portions of the image and not on the uncharged background areas of the image. In addition, toner particles accidentally falling on these non-image areas are physically removed therefrom by the electrostatic attraction of carrier particles which pass in close proximity to these unbound toner particles. The result of this development process is an excellent background-free copy of the electrostatic image made up of the toner particles electrostatically clinging to the image surface. As a general rule when any one of these development processes is used with a reusable xerographic plate, such as an amorphous selenium xerographic plate, the toner particle image is transferred to and fixed on a second layer such as a paper sheet in contact with the toner image by adhesive transfer, or by electrostatic transfer as described in U.S. Patent 2,576,047 to Schaffert. After the image is transferred from the surface of the amorphous selenium xerographic plate, the plate surface may be cleaned and it is then ready for reuse in a subsequent xerographic cycle. The toner resins are usually thermoplastics selected to have melting points significantly above any ambient temperatures which might be encountered (generally running above 180° F.) and these are fixed to the paper in most cases by radiant heat fusing.

Most other electrostatographic techniques use the above described or similar development methods employing the same type of marking material or toner, and differ only in the mode of forming the latent electrostatic charge pattern which is developed. (See, for example, U.S. Patents 2,576,047 to Schaffert and 3,064,259 to Schwertz.) In another technique, for example, in U.S. Patent 3,081,698 to Childress, a conductive screen with a plurality of apertures which define the image area to be reproduced is spaced opposite a conductive backing electrode and a potential is applied between this backing electrode and the screen such that when finely divided electrostatographic toner particles smaller than the apertures in the screen are applied to the surface of the screen opposite the backing electrode, the electrostatic field set up by the potential source causes the particles to move through the apertures in the screen to form a toner image on the backing electrode in the configuration of the apertures on the screen. Various surfaces may be interposed between the screen and the backing electrode so that the particle image may be intercepted and formed on such interposed surfaces. Regardless of the surface upon which the toner image is deposited, it may be fixed in place upon that surface or transferred to another surface and fixed thereon.

The common feature of all of these electrostatographic systems is that they employ the line of force from an electric field to control the deposition of finely divided, marking material or toner on a surface, thus forming an image with the toner particles.

In addition to the developing powder or toner materials described in the original Carlson patent, a number of other toner materials have been developed which are especially valuable for use in the newer development techniques including the cascade technique described immediately 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. Patent 2,659,670 to Copley which describes a toner resin of rosin-modified phenolformaldehyde, U.S. Reissue 25,136 to Carlson which describes a xerographic toner employing a resin of styrene homopolymers, copolymers and polymer blends, U.S. Patent 3,079,342 to Insalaco describing a plasticized styrene-methacrylate copolymer resin.

In the past, these toners have generally been prepared by thoroughly mixing the softened resin and pigment to form a uniform dispersion as by blending these ingredients in a rubber mill or the like and then pulverizing this material to form it into small particles. Most frequently, this division of the resin-pigment dispersion has been made by jet pulverization of the material. Although this technique of toner manufacture has produced some very excellent toners, it does tend to have certain shortcomings. For example, it generally produces a rather wide range of particle sizes in the toner particles. Although the average particle size of toner made according to this technique generally ranges between about 5 and about 10 microns, individual particles ranging from sub micron in size to above 20 microns are not infrequently produced. Furthermore, this is a batch process which tends to be slow, expensive, noisy and dusty. In addition, this technique of toner production imposes certain limitations upon the material selected for the toner because the resin-pigment dispersion 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 resin-pigment dispersion is sufficiently friable for really high speed pulverizing, it tends to form an even wider range of particle sizes during pulverization including relatively large percentages of fines. In addition, such highly friable materials are frequently subject to further pulverization or powdering when they are employed for developing in xerographic copying apparatus. All other requirements of xerographic developers or toners including the requirements that they be stable in storage, nonagglomerative, have the proper triboelectric properties for developing, form good images, do not film or soil the selenium xerographic plate and have a low melting point for heat fusing are only compounded by the additional requirements imposed by this toner forming process. Since most thermoplastic materials are deficient in one or more of the above areas, there is a continuing need for improved toners and developers.

SUMMARY OF THE INVENTION

It is, therefore, an object of this invention to provide a toner overcoming the above-noted deficiencies.

It is another object of this invention to provide toner particles having improved uniformity of particle size.

It is another object of this invention to provide spherical toner particles which are resistant to agglomeration.

It is another object of this invention to provide toners which are easily removed from reusable xerographic imaging surfaces.

It is another object of this invention to provide toners having high resolution imaging capabilities.

It is another object of this invention to provide a more rapid and economical process for forming toner particles.

It is another object of this invention to provide toners which are resistant to forming films on xerographic imaging surfaces.

It is another object of this invention to provide a xerographic 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 a xerographic toner comprising spherical particles containing a colorant and a resin prepared as a latex in the presence of at least one chain transfer agent. The resin is prepared by aqueous emulsion polymerization techniques, has a second order or glass transition temperature (Tg) of from about 30° C. to about 85° C., and a weight average molecular weight between about 10,000 and about 500,000. A weight average molecular weight within this range is achieved by regulating the relative quantity of organic chain transfer material present during the polymerization of the resin. Regulation of the molecular weight of the resin is desirable to maintain the melting range of the toner resin within the upper fusing limits of xerographic copying and duplicating machines. A resin molecular weight at least about 10,000 prevents the formation of toner fines in automatic machines and improves the resistance of the toner to impaction coating on carrier bead surfaces. In accordance with the present invention, there is provided a new and improved method of electrostatographic toner production capable of producing toner particles with very significantly improved uniformity of molecular weight and particle size. The new toner produced according to this method has also been found to have a unique spherical shape which is particularly desirable in cascade development. In addition, it has been found that this new method of toner production is capable of forming a toner of extremely small particle size. Both the uniformity of particle size and the fineness of particle size which may be achieved in this new method have gone to produce a toner with high resolution capabilities which may be used in virtually any electrostatographic development technique including those described above. The ultimate resolution capability of any electrostatographic system such as xerography is limited by the largest toner particles which are included in the batch of toner being utilized to develop the latent electrostatic image regardless of the particular development technique employed. Thus, even when an optical system and xerographic plate are capable of producing extremely high resolution latent electrostatic images, the overall system resolution is reduced if the latent image is developed with a xerographic toner containing particles of a size larger than the dimensions of any part of the latent image. Accordingly, toner produced by the new method of this invention is superior in two respects for the production of high resolution images. First, it is capable of producing extremely small particle size toner and secondly, it significantly narrows the particle size range of the toner produced thus reducing or completely eliminating any random particles of much larger than average size which might be included in a toner produced by conventional techniques. In addition, the process can be carried out continuously instead of in a batch method and requires the use of little or no explosive or flammable solvents and is not dusty, noisy or otherwise obnoxious.

Basically, the technique of this invention consists of preparing a water latex of the desired resin in the presence of at least one chain transfer agent, blending the water latex with a colorant and then spray drying this combined system to the desired particle size. Although any one of many known resinous developing materials which are electroscopic in nature and which will coalesce on heating in the spray drier may be used to form a water latex, it has generally been found that electrically insulating, water insoluble, thermoplastic, polymeric addition reaction products including for example, those of the Carlson Reissue and Insalaco patents referred to above, form toners having many highly desirable properties for xerographic copying. Different types of addition polymerization resins may, of course, be preferred for other uses. Furthermore, the use of any of these addition polymerization resins generally makes possible a combination of two of the steps in the toner forming process. Thus, by the simple expedient of employing emulsion polymerization of the resin, the water latex is simultaneously formed as the end product of the polymerization technique. The use of emulsion polymerization also lends itself to the formation of a highly stable latex with uniformity of polymer particle dispersion throughout, so that the final particle produced by the spray drying process is of a uniform size. The production of small polymer particles in the emulsion may be accomplished in emulsion polymerization by introducing an organic chain transfer agent and an emulsifier or surfactant, into the emulsion before polymerization. By using a relatively large quantity of surfactant in the water when the monomer is initially stirred into it, a relatively large number of small monomer-swollen micelles is formed in the emulsion which in turn form substantially the same large number of small polymer particles in the emulsion following the addition of the polymerization initiator.

Any suitable vinyl monomer may be employed in the process of this invention. Vinyl monomers may be defined as those monomers containing the characteristic ethylenically unsaturated structure: $>C=C<$, and capable of undergoing addition polymerization. Typical vinyl monomers include: esters of saturated alcohols with mono and polybasic unsaturated acids such as alkyl acrylates and methacrylates, haloacrylates, diethyl maleate, and mixtures thereof; vinyl and vinylidene halides such as vinyl chloride, vinyl fluoride, vinylidene chloride, vinylidene fluoride, tetrafluoroethylene, chlorotrifluoroethylene and mixtures thereof; vinyl esters such as vinyl acetate, unsaturated aromatic compounds such as styrene and various alkyl styrenes, parachlorostyrene, parabromostyrene, 2,4, dichlorostyrene, vinyl naphthalene, paramethoxystyrene and mixtures thereof; unsaturated amides such as acrylamide, methacrylamide and mixtures thereof; unsaturated nitriles such as acrylonitrile, methacrylonitrile, haloacrylonitrile, phenylacrylonitrile, vinylidene cyanide, and mixtures thereof; N-substituted unsaturated amides such as N,N-dimethyl acrylamide, N-methyl acrylamide and mixtures thereof; conjugated butadienes such as butadiene, isoprene and mixtures thereof; unsaturated ethers such as divinyl ether, dially ether, vinyl alkyl ether and mixtures thereof; unsaturated ketones such as divinyl ketone, vinyl alkyl ketone and mixtures thereof; unsaturated aldehydes and acetals such as acrolein and its acetals, methacrolein and its acetals, and mixtures thereof; unsaturated heterocyclic compounds such as vinyl pyridine, vinyl furan, vinyl coumarone, N-vinyl carbazole, and mixtures thereof; unsaturated alicylic compounds such as vinyl-cyclopentane, vinyl-cyclohexane and mixtures thereof; unsaturated thio compounds such as vinyl thioethers; unsaturated hydrocarbons such as ethylene, propylene, coumarone, indene, terpene, polymerizable hydrocarbon fractions, isobutylene and mixtures thereof; allyl compounds such as allyl alcohol, allyl esters, diallyl phthalate, triallylcyanurate and the like. Any suitable homopolymer, copolymer or terpolymer of the above materials may be used in the process of this invention. Polymers of the types above include polyvinyl butyral, copolymers of methacrylic acid with methylmethacrylate, with acrylonitrile or with styrene, copolymer of vinyl acetate with maleic anhydride, copolymer of nitrostyrene with diethylmaleate, copolymers of styrene with acrylic and methacrylic acids and esters, and the like.

Any suitable surfactant of the well-known cationic, anionic and nonionic types may be employed in the process of this invention. Typical examples of surfactants are napthalenic soaps or sulfonates; sulfonation products of glycerides or their fatty acids; sulfonated derivatives of esters of mono- and polyvalent alcohols; esterification products of fatty acid and sulfonated monovalent alcohols; sulfonated derivatives of fatty acid esters, such as the diamyl or dioctyl esters of sodium sulfosuccinic acid; sulfonation products of fatty amides; ketones, aldehydes, and nitriles; sulfonation products of natural and synthetic alcohols; such as alkyl sulfates and sulfonates, phosphoric and pyrophosphoric esters of fatty alcohols, such as the sodium salt of 2-ethyl hexyl phosphate; amino carboxylic acids; sulfonated aromatic hydrocarbons, such as the sodium alkyl aryl sulfates and sulfonates, alkylated aryl sulfonates; sulfonated and chlorosulfonated paraffin hydrocarbons; sulfated and sulfonated derivatives of nonionic compounds such as the sodium alkyl aryl polyether sulfates and sulfonates; aliphatic amines and their derivatives, aromatic amines having fatty chains; fatty amines of aliphatic diamines; quaternary ammonium compounds (bases and halides), such as dimethyl phenyl benzyl ammonium chloride, decyl trimethyl ammonium chloride, dodecyl trimethyl ammonium chloride, tetradecyl trimethyl ammonium chloride, hexadecyl trimethyl ammonium chloride, octadecyl trimethyl ammonium chlorides, amines derived from amino alcohols and their quaternary ammonium derivatives; basic compounds of pyridinium and its derivatives; polypropanol and polyethanol amines, urethanes or basic salts of ethylene diamine; condensation products of fatty substances and their derivatives with ethylene oxide, such as the polyoxalkylene ethers of partial lauric, palmitic, stearic, or oleic acid esters; and condensation products of phenolic compounds having side chains with ethylene oxide such as the condensation product of dodecyl phenol with ethylene oxide. It also may be desirable in some instances to employ two or more surfactants to optimize properties of the emulsion such as stability, micelle control and particle growth. The relative quantity of surfactant employed is preferably less than about 3 percent by weight based on the weight of the total non-aqueous reaction mixture because the resulting toner material possesses greater triboelectric stability under fluctuating ambient humidity conditions. Optimum stability of the emulsion and the resulting toner polymer is achieved when about 0.25 to about 1.5 percent by weight, based on the total weight of the non-aqueous reaction mixture, of surfactant is used.

Any suitable system of catalysis or initiation may be used in the emulsion polymerization process, including, for example, free radical catalysis with a peroxide, a persulfate, an azo compound, or ultraviolet light. With a catalyst such as a peroxide or a persulfate such as ammonium persulfate, the redox form of free radical catalysis in which a water soluble reducing agent such as sodium sulfite, sodium bisulfite or ferrosulfate is included may also be employed so as to allow for more rapid polymerization at relatively lower temperatures. If desired, suitable secondary initiators such as t-butyl hydroperoxide may be added prior to or during the polymerization step to promote complete conversion of the monomer.

Although tap water, having a low polyvalent metal ion content may be employed to form the emulsion, softened or deionized water is preferred because greater control of the emulsion, particularly as to rate of polymerization and prevention of flocculation of the monomer and polymer components, is achieved.

Any suitable chain transfer agent may be employed in the emulsion polymerization process of this invention. Typical chain transfer agents include: hexyl mercaptan, lauryl mercaptan, n-butyl mercaptan, t-butyl mercaptan, n-dodecyl mercaptan, n-amyl mercaptan, ethyl mercaptoacetate, thio beta-naphthol, ethyl thioglycolate, ethanethiol, butanethiol, thiophenol, 3-ethoxypropane thiol, dodecanethiol, diisopropyl xanthogen, pentaphenylethane, and carbon tetrabromide. The sulfur-containing chain transfer agents are preferred because the relative quantity of chain transfer agent necessary to modify the molecular weight of the emulsion polymer is usually less than that required with other chain transfer agents. Satisfactory results are obtained when about 0.5 percent to about 3 percent by weight based on the total weight of the non-aqueous components in the reaction mixture, of the chain transfer agent is employed. As indicated above, regulation of the molecular weight of the polymer is desirable to maintain the melting range of the toner resin below the upper fusing limits of xerographic copying and duplicating machines. A resin weight average molecular weight of at least about 10,000 is desirable to prevent the formation of undesirable toner fines in automatic machines and to improve the carrier bead impaction resistance of the toner. It is well known in the art that toner particles are normally melted or fused to the surface of paper and therefore should flow into the surface of a paper receiving surface when heated to a temperature below the discoloration or char point of the paper. Conventional toner fusing temperatures, as exemplified by the temperatures disclosed in the Carlson Reissue, Copley and Insalaco patents referred to above, range from about 85° C. to about the char point of paper. The char point of paper is, as disclosed by Landrigan in U.S. Patent 2,753,308, approximately 175° C. Toner fusing temperatures as low as about 65° C. are satisfactory. When toner melting ranges are reduced below about 65° C., the tendency of the toner particles to form undesirable agglomerates during handling and storage increases markedly. Vinyl monomers polymerized in the absence of a chain transfer agent often tend to form polymers having undesirably high molecular weights. Toner resins having a weight average molecular weight above about 500,000 tend to resist flowing into the surface of paper receiving sheets and form poorly adhering or unfixed images. By adjusting the relative quantity of a chain transfer agent in a reaction mixture, one may control the average number of monomer units in the ultimate polymer molecules. An increase in the amount of chain transfer agent present will lower the molecular weight of the polymer formed. The relative quantity of chain transfer agent to be used depends upon such factors as the particular chain transfer agent and monomer or monomers employed, the polymerization conditions (e.g., the degree of emulsion agitation and temperature), and the average molecular weight desired. Techniques for determining the approximate concentration of chain transfer agent to be employed to achieve the desired polymer molecular weight as well known and are described, for example, by F. R. Mayo, Journal American Chemical Society, volume 65, page 2324 (1943) and P. J. Flory, Principles of Polymer Chemistry, Cornell University Press, page 138, (1953). The melting or fusing temperatures discussed herein are determined on a Fisher-Johns Melting Point Apparatus.

As is well known to those familar with emulsion polymerization, broadly, this technique involves mixing water, surfactant, initiator, and the monomeric precursor of the polymer to be formed. When this mixing occurs, the surfactant molecules line up in the water phase in orderly groups known as micelles. Some monomer is dissolved in these micelles. In addition, relatively large monomer droplets are stabilized by surfactant action and most frequently also by agitation of the mixture during the polymerization process. These monomer droplets may be thought of as reservoirs of monomer which are distributed later as needed in the polymerization reaction. When initiator diffusing through the water contacts monomer, it can initiate polymerization, assuming the system is at a suitable temperature. As polymerization proceeds in the micelle, the monomer therein is used up. The depleted monomer is replenished by diffusion from the large monomer droplets and gradually the micelles because transformed into monomer swollen polymer particles. Both during and after polymerization, the surfactant is concentrated at the water-polymer interface thereby preventing particle coalescence or coagulation. In forming the toner resins of this invention, the above described chain transfer agent may be employed with any suitable conventional emulsion polymerization process. If desired, conventional buffers such as phosphate, amino acids and polyamides may be added during or subsequent to polymerization. The emulsion may contain between about 10 percent to about 50 percent by weight, based on the total weight of the emulsion of monomer material. A monomer content between about 30 to about 40 percent by weight is preferred because greater emulsion stability is obtained when the emulsion contains less than about 40 percent by weight of monomer and greater polymer yields are achieved when the monomer content is at least about 30 percent by weight.

Any suitable coloring technique may be employed to impart the desired color to the toner resins of this invention prior to drying the aqueous liquor from the system. The colorant used may be either water soluble in which case it may be merely added and dissolved into the reaction mixture or water insoluble dye in which case it may first be placed in an aqueous suspension and then added to the reaction mixture. The colorant may be added to the reaction mixture at any stage of the polymerization process prior to removal of the aqueous liquor. However, care must be taken to avoid the use of colorants which inhibit polymerization if the colorant is to be added prior to polymerization. Accordingly, suitable pigments, dye pigments, water soluble dyes, water insoluble dyes, or any other suitable colorants such as powdered metals may be used. Typical pigments and dyes include: Monastral Green, Celliton Blue, Victoria Green S, Spirit Blue, IRN-100 (iron powder), carbon black, Neutral Red, Congo Red, Titanox A-Lo (an anatase titanium dioxide pigment), Cadmium Yellow, Anthraquinone Red. Any suitable dye or class of dyes may be used to color the suspension. Typical acid dyes include, for example, anthraquinone-C. I. Acid Blue 127, triphenylmethane-C. I. Acid Blue 103, azine-C.I. Acid Blue 98, xanthene-C. I. Acid Violet 9, nitroso-C. I. Acid Green 1, monoazo-C. I. Acid Yellow 29, diazo-C. I. Acid Green 20, xanthene-C. I. Acid Red 92, quinoline-C. I. Acid Yellow 3, disazo-C. I. Acid Orange 79. Typical basic dyes include thiazole-C. I. Basic Yellow 1, ketone imine-C. I. Basic Yellow 2, acridine-C. I. Basic Yellow 4. Typical dispersed dyes include nitroacetamine Yellow 2 RZ-C. I. Disperse Yellow 1, azo-Disperse Red 1, anthraquinone-C. I. Disperse Violet Celanthrene Red, anthraquinone-C. I. Disperse Blue 9, amino ketone-C. I. Disperse Green 1, azo-C. I. Disperse Black 9, C. I. Blacks 18, 19, 16, 1, 7, 12, 24, and 27; and diazo-C. I. Food Black 1. The pigment or dye should be present in a sufficient quantity to render the toner highly colored so that it will form a clearly visible image on a recording member. Preferably, for sufficient color density, the pigment is employed in an amount from about 1 percent to about 20 percent by weight, based on the total weight of the colored toner. If the toner colorant employed is a dye, substantially smaller quantities of colorant may be used.

As discussed above, satisfactory results are obtained with toner resins having a weight average molecular weight between about 10,000 and about 500,000 and a second order glass transition temperature (Tg) between about 30° C. and about 85° C. The second order glass transition temperature may be determined by numerous known techniques, such as for example, by measuring the dynamic modulus of a resin against its temperature and plotting the two as by the torsion pendulum method. As most polymer molecules are heated they first exist in a glassy state and the dynamic modulus remains fairly constant as temperature increases until it reaches the second order or glass transition temperature (Tg) where a sharp increase and peak occurs in the dynamic modulus. Beyond this temperature the polymer exists in a rubbery condition at a lower dynamic modulus than the peak and remains at this level as the temperature is increased over another relatively wide range until it reaches the melting point or first transition temperature (Tm) where a second and generally much larger peak occurs in the dynamic modulus. Beyond this peak, the resin is in a viscous flow condition. Another glass transition measuring technique is described by G. K. Dyvik et al., SPE Transactions, vol. 4, No. 2, (1964). The glass transition temperature of many copolymers may be determined with the Glass Temperature Analyzer, SP-222 available from the special Products Department of the Rohm & Haas Company, Philadelphia, Pennsylvania. Preferably, the emulsion polymerization resins should have a glass transition temperature between about 40° C. to about 80° C. and a weight average molecular weight between about 20,000 and 300,000. Toners containing resins having Tg of at least about 40° C. and a weight average molecular weight of at least about 20,000 exhibit greater resistance to filming on the surface of reusable xerographic plates, reduced tendency to block and agglomerate, and improved resistance to impaction on the surface of carrier beads. Toner resins having a Tg less than about 80° C. and a weight average molecular weight of less than about 300,000 are preferred because less power is necessary to heat fix toners containing these resins to paper. Optimized xerographic characteristics are achieved when the resins have a Tg between about 50° C. and about 75° C. and a weight average molecular weight between about 30,000 and 50,000. Toners having a Tg between about 50° C. and about 75° C. and a weight average molecular weight between about 30,000 and 150,000 possess long life characteristics in automatic copying and duplicating machines and are particularly adapted for use in high speed cascade development processes. Outstanding results are obtained with styrene-alkyl methacrylate copolymers having the above described molecular weight and Tg properties, particularly where the alkyl radical of the methacrylate contains 3 to 6 carbon atoms. Toners containing these copolymers are characterized by extremely long machine life and form excellent dense toner images substantially free of background. Thus, copolymers of styrene and alkyl methacrylates in which the alkyl group contains from 3 to 6 carbon atoms are the preferred resins of this invention.

The spray drying step comprises atomizing the colorant-water latex mixture into small droplets, mixing these with a gas, and holding the droplets in suspension in the gas until evaporation drives off the liquid in the droplets and heat and surface tension forces cause the resin particles in each droplet to coalesce encasing the colorant included in that droplet. Most frequently, spray drying utilizes air as the gas for the drying step. The gas is heated to raise the temperature of the resin particles to a point where they coalesce so that the many small particles originating in any one droplet formed during atomization come together to form a small, hard spherical toner particle which entraps any colorant initially included within that droplet.

Colorant must be added to the reaction mixture prior to the spray drying step. Where the colorant is water insoluble it must, of course be suspended in the reaction mixture. This may be accomplished with greater facility by merely adding a commercially available aqueous suspension of the desired pigment and carefully blending the two together. Commercially available aqueous suspensions of carbon black pigment such as "Aquablak" sold by the Columbian Carbon Company, Inc. are found to be highly acceptable in this regard. Since some of these suspensions are fairly susceptible to "shock" it is preferable to add these pigment suspensions to the aqueous reaction mixture with gentle blending to avoid causing the pigment to come out of suspension. Desirably, the particle size of the pigment or any insoluble colorant added to the reaction mixture in the form of an emulsion or suspension will be significantly smaller than the size of the final toner particle produced, again for the purpose of promoting uniformity of product and to produce encapsulation of the colorant within the final toner particle. It has also been found to be generally desirable to use the smallest pigment size available which is economically feasible since the smaller size pigment tends to make a more stable and uniform suspension, and a more uniformly colored toner particle. Where aqueous suspensions of the desired pigment are not commercially available, these suspensions may be prepared by blending the pigment with water and a suitable surfactant. Water suspensions of other water insoluble, liquid colorants may also be prepared for addition to the aqueous reaction mixture by the same technique. Where water soluble dyes are employed as the colorant, they may either be dissolved directly in the aqueous reaction mixture or first dissolved in water followed by addition of this solution to the aqueous reaction mixture. As discussed above, the colorant may be added to the aqueous reaction mixture prior to the spray drying step and may be before or after the monomer material is polymerized. The colorant is preferably added to the aqueous reaction mixture subsequent to polymerization of the monomer material and more preferably just prior to the spray drying step because greater latitude in choice of colorant is available.

By maintaining uniformity of dispersion of colorant and resin in the water, and controlling solids concentration in the final colorant-water latex mixture, the final particle size of the toner produced may be controlled by merely controlling the size of the droplet produced by the atomizing head in the spray drying equipment. This result is produced because when the percentage of water in each droplet is the same and when the droplets are of the same size, the water removed from each droplet in the drying process is equal, thus leaving an equal amount of resin and colorant to produce the final particle. For optimum spray drying concentrations, the latex solids content is adjusted, for example, by dilution, to a concentration of from about 10 to about 20 percent by weight. When the solids concentration is diluted below about 10 percent by weight, the process becomes less economical. Solids concentrations substantially greater than about 50 precent by weight tend to promote the formation of undesirably large toner particle sizes. Preferably, the number of polymer particles from the latex in any one droplet and consequently, the number included in any one final toner particle is relatively large so that these latex particles tend to form a well shaped, hard toner particle and do a good job of entrapping the colorant included in the spray dried liquid droplets whether the colorant is a water insoluble material in suspension or a water soluble colorant in solution. Thus, the size of the polymer particles employed in the emulsion is directly dependent upon the size of final toner particles desired with a smaller polymer particle size preferred for the production of good toner particles of the smaller sizes. For most purposes, electrostatographic toners have been found to be most effective when they range in size from about .5 to about 80 microns with the size desired depending upon the specific end use of the toner. When it is intended to produce toner particles with a final size below about 20 microns in diameter, it is desirable to keep the polymer particles in the water latex below about 6,000 angstrom units in diameter and when producing toner particles having a diameter in the low end of the .5 to 80 micron diameter range, it is preferable to keep these polymer particles in the latex well below 6,000 angstrom units if possible and preferably in the range of about 1,000 angstrom units or less. A good rule is to make the polymer particles small enough so that a relatively large number of them are included in each final toner particle. In fact, it has generally been found that the size of the polymer particles in the latex can never be too small but that by not exceeding the maximum size limits described above, the colorants tend to be well bound in the toner particles which take on a uniform spherical shape and no free colorant is found in the end product. In addition, the use of smaller polymer particles in the water latex contributes significantly to the stability of the latex. The spherical shape is apparently produced when a large number of small polymer particles are used to form one toner particle because they take on a roughly spherical shape even before they are fully coalesced. When the toner mixtures of this invention are to be employed in cascade development processes, the toner should have an average particle diameter less than about 30 microns and preferably betwen about 5 and about 17 microns for optimum results.

Suitable coated and uncoated carrier materials for cascade and magnetic brush development are well known in the art. The carrier particles may be electrically conductive, insulating, magnetic or non-magnetic, provided that the carrier particles acquire a charge having an opposite polarity to that of the toner particles when brought in close contact with the toner particles so that the toner particles adhere to and surround the carrier particles. When a positive reproduction of 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 its 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 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, 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. Patent 2,618,551; L. E. Walkup et al. in U.S. Patent 2,638,416 and E. N. Wise in U.S. Patent 2,618,552. An ultimate coated carrier particle diameter between about 50 microns to about 1,000 microns is preferred because the carrier particles then possess sufficient density and inertia to avoid 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. Patent 3,186,838. Also, print deletion occurs when carrier beads adhere to xerographic imaging surfaces. Generally speaking, satisfactory results are obtained when about 1 part toner is used with about 10 to about 200 parts by weight of carrier.

The toner compositions of the instant invention may be employed to develop latent electrostatic 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. Patent 2,803,542 to Ullrich, U.S. Patent 2,970,906 to Bixby, U.S. Patent 3,121,006 to Middleton, U.S. Patent 3,121,007 to Middleton, and U.S. Patent 3,151,982 to Corrsin.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following examples further define, describe and compare methods of preparing the toner materials of the present invention and of utilizing them to develop latent images. Parts and percentages are by weight unless otherwise indicated. In the following examples, the unit employed for spray drying is a Bowen Laboratory Spray Drier manufactured by Bowen Engineering Incorporated, Northbranch, New Jersey. This unit is a laboratory size, conical, drier with concurrent air flow and has an interchangeable atomizing head mounted near the top of the drying chamber and fitted inside the drying air distributor ring. Any one of a number of well-known atomizing devices or techniques commonly employed in spray drying apparatus may be employed such as centrifugal or swirl-type pressure nozzles, pneumatic or two fluid atomization in which a jet of the liquid is disintegrated as it leaves the nozzle by a high velocity gas stream, atomization by supersonic vibrations or atomization by impingement of the liquid stream against a solid surface. The atomizer used in the following examples is of the spinning-disc type in which the liquid is broken up by discharging it at a high velocity from the periphery of a rapidly rotating disc. This type of atomizer is preferred where any solids such as a pigment are suspended in the liquid since other atomizing nozzles frequently erode during atomization under friction with these solids at high speeds. With any of these atomizers the size of the final toner particle produced is a function of the concentration of solids in the droplet and the size of droplet produced by the atomizer. Although the droplet size produced by the atomizer is dependent upon different factors for each of the various types of atomizers, it is mainly dependent upon the radius and rotational speed with the spinning disc atomizer described above. Since atomization is a highly complex and imperfectly understood phenomena, the best results may probably be obtained by following empirical data of the type given in the examples below. Unless otherwise indicated, the spinning disc atomizer employed a disc having a radius of one inch operated at 50,000 r.p.m. producing various particle sizes depending mainly upon the solids concentrations in the liquid as indicated in the examples. Other systems may, of course, require modification of the spinning disc radius size, speed and solids concentration to achieve equivalent particle sizes. Once the liquid has been atomized to the proper droplet size, it moves through the heated drying air until the water is driven off by evaporation which is hastened by the high surface to mass ratio of the droplets and the warmth of the air. The time during which these droplets are held in suspension in the drying air is referred to as the "Dwell time." Once the dried toner particles leave the drying air chamber, they must not be so tacky that they tend to stick to the sides of the apparatus or agglomerate in the collecting device. It is generally found that with most of the desirable thermoplastic polymers the desired result may be achieved by maintaining an input drying air temperature such that the particles leaving the spray drier are just below their fusing or caking temperature, while using a higher drying air input temperature which is allowable because evaporation of the water after the initial heating of the droplets tends to cool the coalesced particles. If desirable, the dried toner particles may be quenched as they leave the drying air chamber with a stream of cool air to insure that they do not agglomerate in the collector. This step, however, is unusual and is normally not required with conventional materials. The output of the spray drier is connected to a cyclone-type product collector from which the final dried particles may be taken at the end of the process.

EXAMPLE I

A toner resin is prepared from the following materials:

Material:	Parts by weight
Styrene	65
n-butyl methacrylate	35
Ammonium persulfate	0.5
Sodium meta bisulfite	0.5
Sodium alkyl aryl ether sulfate (27 percent aqueous solution), Triton W-30	2
Lauryl mercaptan	1.2
Deionized water	240

About 120 parts by weight of deionized water and about 2 parts by weight of surfactant are introduced into a a reaction kettle fitted with a water cooled condenser, electric stirrer, inert gas bubbler tube and thermocouple. The apparatus is purged with argon and stirred at a temperature of about 25° C. The monomers and mercaptan are added with continued stirring followed by the introduction of the sodium meta bisulfite dissolved in about 60 parts by weight of water. The ammonium persulfate and about 60 parts by weight of water is then added. The temperature of the reaction mixture is allowed to reach a maximum of about 80° C. and is maintained at this temperature for about two hours with constant stirring. The emulsion is then cooled with stirring and subsequently strained through cheesecloth. A sample of the copolymer produced by this process has a second order glass transition value (Tg) of about 67° C. and a weight average molecular weight of about 180,000. The emulsion is adjusted by the addition of deionized water to a solids content of about 15 percent by weight. A spray drying liquid was made from this emulsion by adding one part by weight of Aquablak 41 for every four parts of the emulsion. Aquablak 41 is a suspension of 25% by weight of a nine millimicron diameter carbon black in water and is available from Columbian Carbon Company. This spray drying liquid was then spray dried with a spinning disc-type atomizer at a pressure of about 75 p.s.i., a feed rate of about 80 milliliters per minute, a drying air input temperature of about 200° F. and an output temperature of about 170° F. A good quality medium-fine powder with the majority of the particles ranging from about 7 to about 11 microns was produced and was found to form good xerographic images which were readily fixed when tested in a conventional cascade xerographic copying machine. Further, no agglomeration of the toner particles is observed after the toner particles are stored in an air circulating oven maintained at a temperature of about 110° F. for about 24 hours.

EXAMPLE II

A toner resin is prepared from the following materials:

Material:	Parts by weight
Styrene	65
n-butyl methacrylate	35
Ammonium persulfate	1
Sodium alkyl arylether sulfate (27 percent aqueous solution)	1
Lauryl mercaptan	1.5
Deionized water	240

About 120 parts by weight of deionized water and about 2 parts by weight of the surfactant are introduced into the reaction vessel of the type described in Example I. The apparatus is purged with carbon dioxide and stirred at room temperature. The monomers and mercaptan are then added with stirring. The resulting mixture is heated to about 75° C. and the ammonium persulfate and remaining water is then added. The reaction is carried out isothermally at about 75° C. for about two and one half hours. The emulsion is then cooled with stirring and strained through a screen. A sample of the copolymer produced by this process has a Tg of about 67° C. and a weight average molecular weight of about 90,000. The emulsion solids content adjustment, carbon black addition and spray drying procedure described in Example I is repeated. The resulting spherical toner particles form excellent high density xerographic images which are easily fixed in a conventional xerographic copying machine. These toners are also highly resistant to the formation of films on the surface of reusable imaging surfaces. No tendency of the toner to form agglomerates is observed when the toner particles are stored in an air circulating oven maintained at a temperature of about 110° F. for about 24 hours.

EXAMPLE III

A toner resin is prepared from the following materials:

Material:	Parts by weight
Styrene	65
n-butyl methacrylate	35
Ammonium persulfate	1
Sodium alkaryl ether sulfate (27 percent aqueous solution)	1
Lauryl mercaptan	3
Deionized water	240

The polymerization procedure described in Example II is repeated with the foregoing ingredients. A sample of the copolymer produced has a Tg of about 67° C. and a weight average molecular weight of about 50,000. The emulsion solids content adjustment, carbon black addition and spray drying procedure described in Example II is repeated. Spherical toner particles exhibiting properties similar to the properties of the toner of Example II is obtained.

EXAMPLE IV

Example II is repeated except that the amount of Aquablak added to the emulsion was reduced by one half. All other conditions are substantially the same. It is found that a good quality toner is still produced having approximately the same particle size with very little decrease if any in the blackness of the particles.

EXAMPLE V

Example IV is repeated except that a double-disc atomizer is employed operating at a feed rate of 1 pound per minute and a speed of 21,000 r.p.m. Under these conditions, it is found that the particles range in size from about 6 to about 8 microns in diameter with good pigmentation. High quality, sharply defined images are obtained when this toner is employed in a conventional xerographic copying device.

EXAMPLE VI

Example V is repeated except that the spray drying liquid contains about 20 percent solids, the air output temperature is about 160° F. and the feed rate is about 1.3 pounds per minute. These conditions are found to produce a black, free-flowing toner most of which range in size from about 5 to about 7 microns in diameter.

EXAMPLE VII

Example VI is repeated except that the drying air input temperature is about 240° F.; the output temperature is about 170° F. and the feed rate is about 2.5 pounds per minute. The particles produced range in size from about 7 to about 11 microns for the most part.

Above Examples V, VI, and VII are carried out in a Bowen seven foot spray drier.

EXAMPLE VIII

In this example, an emulsion is made and pigmented as described above in connection with Example II except that the spray drying liquid formulated is diluted down to about 10 percent solids and spray dried with a pneumatic atomizer at a feed rate of about 80 milliliters per minute and a nozzle pressure of about 75 p.s.i. The dryer is operated with an air input temperature of about 180° F. and an output temperature of about 150° F. Spherical particles are produced which for the most part are found to be approximately one micron in diameter.

EXAMPLE IX

A sample of the emulsion described in Example III is adjusted to make up a spray drying liquid about 12.5 percent by weight of solids. To about 102 grams of the resulting spray drying liquid is added about 11 grams of Aquablak 15, a water suspension of about 20 millimicron diameter carbon black containing about 30 percent by weight of the carbon black. This spray drying mixture is spray dried using a spinning disc atomizer operated with a feed rate of about 80 milliliters per minute, a nozzle pressure of about 100 pounds per square inch, a drying air input temperature set at about 190° F.; and an output air temperature measured at about 110° F. Spherical particles are produced most of which are in about the 5 to 7 micron range. Again, it was found that good xerographic images are produced the toner is tested in a conventional xerographic copying apparatus.

EXAMPLE X

A toner resin is prepared from the following materials:

Material:	Parts by weight
Styrene	70
Vinyl acetate	30
Ammonium persulfate	1
Dioctyl ester of sodium sulfosuccinic acid (Aerosol OT)	2.5
Lauryl mercaptan	1
Distilled water	190

About 100 parts by weight of the distilled water and about 2.5 parts by weight of the surfactant are introduced into the reaction vessel of the type described in Example I. The apparatus is purged with nitrogen and stirred at room temperature. The monomers and mercaptan are then added with stirring. The resulting mixture is heated to about 75° C. and the ammonium persulfate and remaining water is added. The reaction is carried out isothermally at about 75° C. for about three hours to insure substantially complete conversion of the monomers. The emulsion is then cooled with stirring and strained. A sample of the copolymer produced has a Tg of about 76° C. and a molecular weight of about 175,000. The emulsion solids content adjustment, carbon black addition and spray drying procedure described in Example I is repeated. The resulting spherical toner particles form good xerographic images and fuse readily under conventional toner fusing conditions. No tendency of the toner to form agglomerates is observed when the toner particles are stored in an air circulating oven maintained at a temperature of about 110° F. for about 24 hours.

EXAMPLE XI

A toner resin is prepared from the following materials:

Material:	Parts by weight
Vinyl acetate	20
Vinyl chloride	80
Ammonium persulfate	0.5
Sodium thiosulfate	0.3
Sodium lauryl sulfate	3
Thiophenol	1
Deionized water	160

About 100 parts by weight of the deionized water and about 3 parts by weight of the surfactant are introduced into a reaction vessel of the type described in Example I. The apparatus is purged with argon and stirred at about 25° C. The monomers and thiophenol are then added with stirring. The resulting mixture is then mixed with the remaining ingredients. The reaction is carried out under pressure to a maximum exotherm of about 70° C. for about three hours to insure substantially complete conversion of the monomers. The emulsion is then cooled with stirring and strained. A sample of the copolymer produced has a Tg of about 72° C. and a weight average molecular weight of about 130,000. The emulsion solids content adjustment, carbon black addition and spray drying procedure described in Example II is repeated. The resulting spherical toner particles form good xerographic images and fuse readily under conventional toner fusing conditions. No tendency of the toner to form agglomerates is observed when the toner particles are stored in an air circulating oven maintained at a temperature of about 110° F. for about 24 hours.

EXAMPLE XII

A toner resin is prepared from the following materials:

Material:	Parts by weight
Vinyl chloride	40
Methyl acrylate	60
Hydrogen peroxide (3 percent by weight aqueous solution)	30
Peracetic acid (10 percent by weight aqueous solution)	10
Sodium salt of alkyl aryl polyether sulfonate (72 percent mixture), Tamol SN	2
Thio-beta-naphthol	0.6
Deionized water	150

About 90 parts by weight of the deionized water and about 2 parts by weight of the surfactant are introduced into the reaction vessel of the type described in Example I. The apparatus is purged with carbon dioxide and stirred at room temperature. The monomers and mercaptan are then added with stirring. The resulting mixture is heated to about 60° C. and the remaining ingredients are added. The reaction is carried out isothermally at about 60° C. for about two hours to insure substantially complete conversion of the monomers. The emulsion is then cooled with stirring and strained. A sample of the copolymer produced has a Tg of about 34° C. and a weight average molecular weight of about 250,000. The emulsion solids content adjustment, carbon black addition and spray drying procedure described in Example II is repeated. The resulting spherical toner particles form good xerographic images and fuse readily under conventional toner fusing conditions. No tendency of the toner to form agglomerates is observed when the toner particles are stored in an air circulating over maintained at a temperature of about 110° F. for about 24 hours.

EXAMPLE XIII

A toner resin is prepared from the following materials:

Material:	Parts by weight
Styrene	65
n-butyl methacrylate	35
Ammonium persulfate	0.5
Sodium metabisulfate	0.5
Dioctyl ester of sodium sulfosuccinic acid	1
Hexyl mercaptan	2
Distilled water	240

About 110 parts by weight of the distilled water and about 1 part by weight of the surfactant are introduced into the reaction vessel of the type described in Example I. The apparatus is purged with nitrogen and stirred at 25° C. The monomers and mercaptan are then added with stirring. The remaining ingredients are then added with continued stirring. The reaction is allowed to reach a maximum of about 80° C. and is then maintained at 80° C. for about four hours to insure substantially complete conversion of the monomers. The emulsion is then cooled with stirring and strained. A sample of the copolymer produced has a Tg of about 670° C. and a weight average molecular weight of about 90,000. The emulsion solids content is adjusted with distilled water to about 10 percent by weight of solids. About 10 percent by weight, based on the weight of the latex solids, of Eosine bluish dye is added to the emulsion and the resulting mixture is agitated with a Bronson Sonifier ultrasonic mixer. The mixture is then spray dried as described in Example I. The resulting spherical toner particles form excellent xerographic images and fuse readily under conventional toner heat fusing conditions. No tendency of the toner agglomerates is observed when the toner particles are stored in an air circulating oven maintained at a temperature of about 110° F. for about 24 hours.

EXAMPLE XIV

A toner resin is prepared from the following materials:

Material:	Parts by weight
Vinylidene chloride	20
Vinyl chloride	80
Ammonium persulfate	0.5
Sodium metabisulfite	0.5
Sodium lauryl ethoxylate sulfate (28 percent mixture), Supex ES	6
n-butyl mercaptan	1.5
Deionized water	150

About 75 parts by weight of the deionized water and about 6 parts by weight of the surfactant are introduced into a pressure reaction vessel similar to the type described in Example I. The apparatus is purged with argon and stirred at room temperature. The monomers and mercaptan are then added with stirring. The resulting mixture is heated to about 25° C. and the remaining ingredients are added. The reaction is carried out under pressure and allowed to reach a maximum temperature of about 70° C. The temperature is maintained at 70° C. for about four hours to insure substantially complete conversion of the monomers. The emulsion is then cooled with stirring and strained. A sample of the copolymer produced has a Tg of about 51° C. The emulsion solids content adjustment, carbon black addition and spray drying procedure described in Example V is repeated. The resulting spherical toner particles form good xerographic images and fuse readily under conventional toner fusing conditions. No tendency of the toner to form agglomerates is observed when the toner particles are stored in an air circulating oven maintained at a temperature of about 110° F. for about 24 hours.

EXAMPLE XV

A toner resin is prepared from the following materials:

Material:	Parts by weight
Styrene	50
Ethyl methacrylate	50
Ammonium persulfate	2
Aerosol MA (80 percent by weight mixture)	1.5
Lauryl mercaptan	2
Distilled water	240

About 140 parts by weight of the distilled water and about 2 parts by weight of the surfactant are introduced into the reaction vessel of the type described in Example I. The apparatus is purged with argon and stirred at room temperature. The monomers and mercaptan are then added with stirring. The resulting mixture is heated to about 80° C. and the ammonium persulfate and remaining water is added. The reaction is carried out isothermally at about 80° C. for about three hours to insure substantially complete conversion of the monomers. The emulsion is then cooled with stirring and strained. A sample of the copolymer produced has a Tg of about 82° C. and a weight average molecular weight of about 40,000. The emulsion solids content adjustment, carbon black addition and spray drying procedure described in Example I is repeated. The resulting spherical toner particles form good xerographic images and fuse readily under conventional toner fusing conditions. No tendency of the toner to form agglomerates is observed when the toner particles are stored in an air circulating oven maintained at a temperature of about 110° F. for about 24 hours.

EXAMPLE XVI

A toner resin is prepared from the following materials:

Material:	Parts by weight
Styrene	80
Ethyl acrylate	40
Potassium persulfate	1
Octyl phenyl polyethoxy ethanol (70 percent by weight mixture), Triton X 405	3
Lauryl mercaptan	2
Deionized water	240

About 100 parts by weight of the deionized water and about 3 parts by weight of the surfactant are introduced into the reaction vessel of the type described in Example I. The apparatus is purged with carbon dioxide and stirred at room temperature. The monomers and mercaptan are then added with stirring. The resulting mixture is heated to about 75° C. and the potassium persulfate and remaining water is added. The reaction is carried out isothermally at about 75° C. for about four hours to insure substantially complete conversion of the monomers. The emulsion is then cooled with stirring and strained. A sample of the copolymer produced has a Tg of about 41° C. and a weight average molecular weight of about 85,000. The emulsion solids content adjustment, carbon black addition and spray drying procedure described in Example II is repeated. The resulting spherical toner particles form good xerographic images and fuse readily under conventional toner fusing conditions. No tendency of the toner to form agglomerates is observed when the toner particles are stored in air circulating oven maintained at a temperature of about 110° F. for about 24 hours.

EXAMPLE XVII

A toner resin is prepared from the following materials.

Material:	Parts by weight
Styrene	65
n-butyl methacrylate	35
Ammonium-persulfate	0.5
Sodium bisulfite	7.5
Sodium salt of alkyl aryl polyether sulfonate, Triton X-200	4
Dodecyl mercaptan	0.5
Carbon black (15 percent by weight aqueous mixture) Aquablack U	33
Deionized water	160

About 100 parts by weight of the deionized water and about 4 parts by weight of the surfactant are introduced into the reaction vessel of the type described in Example I. The apparatus is purged with nitrogen and stirred at 25° C. The monomers and mercaptan are then added with stirring. The Aquablack U mixture is added with continued stirring following by addition of the remaining ingredients. The reaction is allowed to reach a temperature of about 75° C. where it is maintained for about two hours to insure substantially complete conversion of the monomers. The emulsion is then cooled with stirring and strained. A sample of the copolymer produced after removal of the carbon black has a Tg of about 67° C. The emulsion is diluted with deionized water to a solids content of about 20 percent by weight and the spray drying procedure described in Example VI is repeated. The resulting spherical toner particles form good xerographic images and fuse under conventional toner fusing conditions. No tendency of the toner to form agglomerates is observed when the toner particles are stored in an air circulating oven maintained at a temperature of about 110° F. for about 24 hours.

It is to be understood that the specific designations given for the monomeric units contained in the resins of this invention represent the vast majority of the units present, but do not exclude the presence of other monomeric units or reactants than those which have been shown. For example, some commercial materials such as the polystyrene may contain minor amounts of homologues. Any minor amount of such substituents may be present in the materials of this invention.

Although specific materials and conditions are set forth in the foregoing examples, these are merely intended as illustrations of the present invention. Various other suitable toner resins, additives, colorants, and other components, such as those listed above may be substituted for those in the examples with similar results. Other materials such as conventional shortstop materials (e.g., sodium polysulfide, sodium dimethyldithiocarbamate, hydroquinone and phenylhydrazine) may be added to sensitize, synergize, or otherwise improve the handling 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. The method of forming spherical xerographic toner particles comprising the steps of preparing an aqueous emulsion comprising water, surfactant, vinyl monomer material and at least one chain transfer agent, converting said emulsion to a latex by polymerizing said vinyl monomer material in the presence of an initiator to form a polymer having a Tg value of from about 30° C. to about 85° C. and a weight average molecular weight between about 10,000 to about 500,000, adding a colorant to said latex to form a spray drying mixture, atomizing said spray drying mixture to form small droplets suspended in a gas, maintaining said droplets in suspension in said gas while applying heat until said water in said droplets is caused to coalesce and entrap said colorant included in said droplets, and collecting the resulting dry toner particles.

2. The method of forming spherical toner particles according to claim **1** wherein said emulsion contains between about 0.5 to about 3 parts by weight, based on the total weight of the non-aqueous materials in said emulsion, of said chain transfer agent.

3. The method of forming spherical toner particles according to claim **2** wherein said chain transfer agent is a sulfur containing compound.

4. The method of forming spherical toner particles according to claim **1** wherein said emulsion contains less than about 3 percent by weight, based on the total weight of the non-aqueous materials in said emulsions, of said surfactant.

5. The method of forming spherical toner particles according to claim **1** wherein said polymer has a weight average molecular weight between about 20,000 and about 300,000.

6. The method of forming spherical toner particles according to claim **5** wherein said polymer has a weight average molecular weight between about 30,000 and about 150,000.

7. The method of forming spherical toner particles according to claim **1** wherein said polymer has a Tg between about 40° C. and about 80° C.

8. The method of forming spherical toner particles according to claim **1** wherein said polymer has a Tg between about 50° C. and about 75° C.

9. The method of forming spherical toner particles according to claim **1** wherein said polymer has a fusing temperature between about 65° C. and about 175° C.

10. The method of forming spherical toner particles according to claim **1** wherein said spray drying mixture contains less than about 20 percent by weight, based on the total weight of non-aqueous materials in said emulsion, of said colorant.

11. The method of forming spherical xerographic toner particles according to claim **1** wherein said polymer is a copolymer of a styrene monomer and an alkyl methacrylate monomer.

12. The method of forming spherical xerographic toner particles according to claim **11** wherein the alkyl group of said alkyl methacrylate contains from 3 to 6 carbon atoms.

13. The method of forming spherical toner particles according to claim **1** including spray drying said spray drying liquid to a particle size such that the solids contained in each droplet will produce a final solid particle less than about 20 microns in diameter.

14. The method of forming spherical toner particles comprising the steps of preparing an aqueous emulsion comprising water, surfactant, a vinyl monomer material, at least one chain transfer agent and up to about 20 percent by weight, based on the total weight of non-aqueous material in said emulsion, of a colorant, converting said emulsion to a latex by polymerizing said vinyl monomer material in the presence of an initiator to form a polymer having a Tg value of from about 30° C. to about 85° C., a weight average molecular weight between about 10,000 to about 500,000 and a fusing temperature between about 65° C. to about 175° C., forming a spray drying mixture having a solids content between about 10 percent to about 20 percent by weight, based on the total weight of said spray drying mixture, atomizing said spray drying mixture to form small droplets suspended in a gas, said droplets having a size such that said solids contained in each of said droplets will produce a final solid particle less than about 20 microns in diameter, maintaining said droplets in suspension in said gas while applying heat until said water in said droplets is caused to coalesce and entrap said colorant included in said droplets, and collecting the resulting dry toner particles.

15. The method of forming spherical xerographic toner particles according to claim **14** wherein said spray drying liquid is atomized by directing a stream of said spray drying liquid against a rapidly rotating disk.

16. The method of forming spherical xerographic toner particles according to claim **14** wherein said polymer is a copolymer of a styrene monomer and an alkyl methacrylate monomer.

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