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SPRAY DRIED LATEX TONERS

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This invention relates in general to electrostatography and in particular to an electrostatographic developing material and a method for its production.

Electrostatography 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 material, 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 accidently 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 zerographic 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, by electrostratic 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 zerographic 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 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 lines 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 phenol-formaldehyde, U.S. Reissue 25,136 to Carlson which describes a xerographic toner employing a resin of styrene polymers and copolymers and 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, non-agglomerative, 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.

Now 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 particle size. Toner produced according to this new 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 blending a water latex of the desired toner resin with a colorant and then spray drying this combined system to the desired particle size. The spray drying step consists of atomizing the colorant-water latex blend 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. The colorant used may be either water soluble in which case it may be merely added and dissolved into the resin latex or water insoluble dye in which case it may first be placed in an aqueous suspension and then added to the resin latex. 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), 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 nitro-acetamine Yellow 2 RZ—C.I. Disperse Yellow 1, azo—C.I. Disperse Orange 3, 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.

By maintaining uniformity of dispersion of colorant and resin in the water, and controlling solids concentration in the final colorant-water latex blend, 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. 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 and even before they are fully coalesced.

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 the water latex, it has generally been found that electrically insulating, water insoluble, thermoplastic, polymers including for example, those of the Copley, Carlson, and Insalaco patents referred to above, form toners having many highly desirable properties for xerographic copying. Different types of resins may, of course, be preferred for other uses. Furthermore, the use of any of these polymers which can be formed by addition polymerization generally makes possible a combination of two of the steps in the toner forming process. Thus, by the simple expedient of employing emulsion polgymerization 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 the use of a relatively high quantity of emulsifier or surfactant, present in the emulsion before polymerization. By using this 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 the same large number of small polymer particles in the emulsion following the addition of the polymerization initiator.

Any suitable natural, modified natural or synthetic resin may be used in the process of this invention. Typical synthetic polymers include vinyl-type polymers having the characterisitic monomeric structure: $>C=C<$, and made, for example, from the following vinyl monomers: 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, alpha-methyl styrene 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, diallyl 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, vinylcoumarone, N-vinyl carbazole, and mixtures thereof; unsaturated alicyclic 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 mixtures thereof; as well as condensation polymers including polyesters, such as linear, unsaturated and alkyd types made, for example, by reacting a difunctional acid or anydride such as phthalic, isophthalic, terphthalic, malic, maleic, citric, succinic, glutoric, adipic, tartaric, pimelic, suberic, azelaic, sebacic and camphoric with a polyol such as glycerine, ethylene glycol, propylene glycol, sorbitol, mannitol, pentaerythritol, diethylene glycol and polyethylene glycol; polycarbonates such as bisphenol esters of carbonic acid; polyamides such as those made by reacting diamines with dibasic acids where the diamines contain from 2 to 10 carbon atoms and the acids contain from 2 to 18 carbon atoms; polyethers such as the epoxy type made, for example, by condensing epichlorohydrin with any one of bisphenol A, resorcinol, hydroquinone, ethylene glycol, glycerol, or other hydroxyl containing compounds; other polyethers made, for example, by reacting formaldehyde with difunctional glycols; polyurethanes prepared, for example, by reacting a diisocyanate such as toluene-2,4-diisocyanate methylene bis (4-phenylisocyanate), bitalylene diisocyanate, 1,5-naphthalene diisocyanate, and hexamethylene diisocyanate with a dihydroxy compound; phenol aldehyde resins made, for example, by condensing resorcinol, phenol or cresols with formaldehyde, furfural or hexamethylene tetramine; urea formaldehyde; melamine formaldehyde; polythioethers; polysulfonamides; alkyl, aryl and alkaryl silicones, etc.

Any suitable mixture, 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 methymethacrylate, 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, etc.

Typical natural and modified natural resins include rosin, hydrogenated rosin, waxes, gums, fossil resins, protein resins such as zein, asphaltum and others.

Although most of the vinyl-type polymers may be conveniently made in a water suspension directly by emulsion polymerization, any of the resins may be emulsified in water, for example, either by first dissolving them in a small amount of an organic solvent and then emulsifying the solution in water or by freeze grinding the resin and suspending the resultant particles in water with a surfactant.

Rather than forming the polymer latex by emulsion polymerization techniques, the process may begin with a commercially available polymer latex having the desired characteristics such as a Pliolite Resin latex of the styrene-butadiene copolymer type (high styrene) available from the Goodyear Tire and Rubber Company.

At any event, once the proper latex is in hand, colorant must be added to it prior to the spray drying step. Where the colorant is water insoluble it must, of course, be suspended in the latex. This may be accomplished with greatest 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 pigments may be purchased under the tradename "Aquablak" from Columbia and Carbon Company and were 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 water latex 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 latex 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 later addition to the water latex by the same technique. Where water soluble dyes are employed as the colorant, they may either be dissolved directly in the water latex or first dissolved in water followed by addition of this solution to the latex.

In the following examples, the unit employed for spray drying was the Bowen Laboratory Spray Drier manufactured by Bowen Engineering Incorporated, North Branch, N.J. This unit is a lab 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 was 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 has generally been 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. Where for some reason a resin is employed which becomes tacky at low temperatures, relatively close to room temperature, it may be desirable to quench the dried toner particles as they leave the drying air chamber with a stream of cold air so that they do not agglomerate in the collector. This step, however, is unusual and is 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

An emulsion of a 65/35% copolymer of styrene and N-butyl methacrylate was made up by emulsion polymerization. The emulsion contained 15% solids 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 75 p.s.i., a feed rate of 80 milliliters per minute, a drying air input temperature of 200° F. and an output temperature of 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 xerographic copying machine.

Example II

Example I was repeated except that the amount of Aquablak added to the emulsion was cut in half. All other conditions were kept the same, and it was found that a good quality toner was still produced of about the same particle size with very little decrease if any in the blackness of the particles.

Example III

Example II was repeated except that a double-disc atomizer was employed operating at a feed rate of 1 pound per minute and a speed of 21,000 r.p.m. Under these conditions, it was found that the particles ranged in size from 6 to 8 microns in diameter with good pigmentation. They also produced good quality images when employed in a conventional xerographic copying device.

Example IV

Example III was repeated except for the fact that the spray drying liquid contained 20% solids rather than 15% and the drying air input temperature was 200° F. with air output temperature 160° F. and a feed rate of 1.3 pounds per minute. These conditions were found to produce a black, free-flowing toner most of which ranged in size from 5 to 7 microns in diameter.

Example V

Example IV was repeated except for the fact that the drying air input temperature was raised to 240° F.; output temperature to 170° F. and feed rate was increased to 2.5 pounds per minute. The particles produced ranged in size from 7 to 11 microns for the most part.

Above Examples III, IV, and V were carried out in a Bowen seven foot spray drier.

Example VI

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

Example VII

A spray drying liquid was made up with 102 grams of a 65–35 styrene-N-butyl methacrylate copolymer and containing 12.5% by weight of solids. To this there was

added 11.33 grams of Aquablak 15, a water suspension of a 20 millimicron diameter carbon black containing 30% by weight of the carbon black. This spray drying liquid was spray dried using a spinning disc atomizer operated with a feed rate of 80 milliliters per minute, a nozzle pressure of 100 pounds per square inch with the drying air input temperatures set at 190° F.; and the output air temperature measured at 110° F. Spherical particles were produced most of which were in the 5 to 7 micron range and here again, it was found that the toner produced good xerographic images when tested in a conventional xerographic copying apparatus.

Example VIII

A spray drying liquid was prepared by blending 173 milliliters of Saran latex F–122 containing 90 grams of solids with 33.3 grams of the Aquablak 15 carbon black suspension, described above, containing 10 grams of solids. The Saran latex is made from a polyvinylidene chloride polymer. This spray drying liquid was spray dried using a spinning disc atomizer operated at a feed rate of 134 milliliters per minute with a nozzle pressure of 100 pounds per square inch and with drying air input temperature at 272° F. and output temperature 151° F. Spherical particles were produced of medium to high black color having a particle size ranging for the most part between 9 and 13.5 microns in diameter.

What is claimed is:

1. The method of forming finely divided electrostatographic toner particles including electroscopic resin and a colorant comprising suspending small particles of said resin in water to form a resin suspension, adding a colorant to said suspension, atomizing said suspension to form small droplets suspended in a gas, and holding said droplets suspended in said gas while heating until the water in each droplet is driven off by evaporation and said resin particles are caused to coalesce, entrapping the included colorant in each droplet, and then collecting the resultant dry toner particles.

2. A method according to claim **1** in which said resin is dissolved in a solvent prior to suspension in water.

3. A method according to claim **1** including the step of suspending said resin in water by emulsifying its monomeric precursor in water and then polymerizing said precursor.

4. A method according to claim **1** in which the step of adding a colorant consists of suspending a substantially water insoluble pigment in said resin suspension.

5. A method according to claim **1** in which the step of adding a colorant to said resin suspension consists of dissolving a water soluble dye therein.

6. The method of making electrostatographic toners comprising adding a colorant to a polymer latex to form a spray drying liquid, atomizing said spray drying liquid to a particle size such that the solids contained in each droplet will produce a final solid particle in the range of from about .5 to about 80 microns, holding said atomized droplets suspended in a gas while heating until the water in the latex is driven off by evaporation and the polymer particles from the latex in each droplet are caused to coalesce around the colorant therein and then collecting the dried particles.

7. A method according to claim **6** in which the atomizing step consists of forming droplets of a size such that the solids contained in each droplet will form a final solid particle in the range from about .5 to about 25 microns in diameter.

8. The method according to claim **7** including using a polymer latex containing polymer particles having a diameter of less than about 6,000 angstrom units.

9. The method according to claim **7** including using a polymer latex containing polymer particles having a diameter of less than about 1,000 angstrom units.

10. The method according to claim **6** including the additional step of quenching the dried particles after evaporation and polymer particle coalescence.

11. The method of claim **6** wherein said spray drying liquid is atomized by directing a stream of said liquid against a rapidly rotating disk.

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