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(54) ELECTROSTATOGRAPHIC TONER

(71) We, XEROX CORPORATION of Rochester, New York State, United States of America, a Body Corporate organized under the laws of the State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to electrostatography and more particularly to improved electrostatographic developing materials, their manufacture and use.

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

ment may be substituted for the foregoing heat fixing steps.

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

Another method of developing electrostatic images is the "magnetic brush" process as disclosed, for example, in U.S. Patent No. 2,874,063. In this method, a developer material containing toner and magnetic carrier particles is carried by a magnet. The magnetic field of the magnet causes alignment of the magnetic carrier into a brush-like configuration. This "magnetic brush" is engaged with the electrostatic image-bearing surface and the toner particles are drawn from the brush to the latent image by electrostatic attraction.

Still another technique for developing electrostatic latent images is the "powder

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cloud" process as disclosed, for example, by C. F. Carlson in U.S. Patent No. 2,221,776. In this method, a developer material comprising electrically charged toner particles in a gaseous fluid is passed adjacent the surface bearing the latent electrostatic image. The toner particles are drawn by electrostatic attraction from the gas to the latent image. This process is particularly useful in continuous tone development.

Other development methods such as "touchdown" development, as disclosed by R. W. Gundlach in U.S. Patent No. 3,166,432 may be used where suitable.

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 zerographic 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 zerographic plate and have a low melting point for heat fusing are only compounded by the additional requirements imposed by this toner forming process.

Another method of toner formation 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 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 the 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. Spray dried toners are not totally satisfactory as it is difficult to completely remove all the solvent and the solvent which remains in the toner particles acts to affect triboelectric properties and contribute to blocking of the toner when in use.

In U.S. Patent 3,391,082 to Maclay, it is proposed that toner be formed directly from an emulsion polymerization system. However, this method is not totally satisfactory as the toner comprises agglomerates of the small latex (0.03 to 0.25 micron) particles the total drying of the system is difficult leading to blocking problems and also voids in the particles may cause structural weakness and uneven triboelectric properties.

It has been proposed in United Kingdom Patent 1,319,815 that toner be prepared directly from the monomer by polymerization of the monomer in toner sized particles containing a colorant. The method of the British patent comprises preparing a kneaded oil phase component made up of one or more liquid resin monomers, coloring material, the polymerization initiator and a finely-divided inorganic dispersion stabilizer such as a metal powder or inorganic salt or oxide and a polar resinous additive which is soluble in a monomer. After suspension polymerization of the monomer, if required, the finely-divided dispersion stabilizer is removed by dissolution in an acid and the polymer particles are removed from the aqueous phase and dried to produce toner. However, this process is not totally successful as it requires a high ratio of inorganic stabilizer which needs to be removed or it affects the quality of the toner. Further the particles recovered contain an unacceptably great number of particles which are either larger or smaller than the size range pre-

ferred for electrophotographic use. Further, the removal of the inorganic stabilizer adds a process step thereby minimizing the advantage of forming a toner in one operation from the monomer. The process in any case often results in incomplete polymerization that leaves residual monomer that affects the triboelectric, blocking and fixing properties of the toner. This incomplete polymerization of the monomer is theorized as caused by the pigment inhibiting polymerization. The similar type Maeda et al process, U.S. 3,634,251, also entails the removal of the inorganic component and problems of incomplete polymerization.

A method of producing small methyl methacrylate beads is disclosed in U.S. Patent 2,701,245 to Lynn. This process uses large amounts of wetting agent, a short period of mixing to size the monomer and does not agitate during polymerization. However, this process does not produce colored beads and the large amount of wetting agent required leaves impurities very undesirable in toners and further the toner has a wide range of particle sizes.

A *Journal of Applied Polymer Science* article at Volume 16, pages 1867 and 1868 (1972), discloses that polymerization of small particle size polymers may be carried out after sizing by high speed stirring of a paddle stirrer. However, the article indicates that control of sizing is difficult and does not deal with the complications caused by introduction of colorant into the system.

It has also been proposed that a suspension polymerization process similar to the above referenced British patent but not making use of an inorganic stabilizer be carried out to produce an encapsulated toner. This process is performed generally by mixing a monomer, a colorant and an initiator to form an oil soluble organic phase; dispersing this oil soluble phase in controlled size between 5 to 20 microns in a water phase, employing a suspending agent, for example polyvinyl alcohol; polymerizing, employing conventional suspension polymerization techniques; introducing a second monomer which is allowed to diffuse into the first polymer and consequently swells the polymer; introducing a water soluble initiator; and heating this reaction mixture to effect polymerization of the second monomer and form the desired toner. It is found that the second initiator, the water soluble initiator, generates a free radical which attacks the surface of the swollen polymer particle and promotes polymerization at the surface by reacting with monomer at the surface thereby decreasing the monomer concentration and causing the transport of monomer to the surface by diffusion. The process is found to be self terminating when the total amount of sorbed monomer has been converted to

polymer at the surface, thus providing an encapsulated toner. However, while this process may be used to produce encapsulated toners, it still does not provide an acceptable method for producing toners which are not encapsulated and which may withstand the abrasion, stress and humidity variation to which toners are subject in ordinary development systems.

A difficulty with suspension polymerization processes is that it is difficult to maintain the toner particle size within the range of about 5 to 30 microns in large suspension polymerization equipment. To obtain particle sizes in the 10 microns range requires stirrer speeds in excess of 1,000 r.p.m. In view of the high stirring speeds, the design of large reactors becomes increasingly difficult as size increases. Large high speed reactors are much more expensive to design and operate than a normal suspension polymerization reactor that operates at the normal about 75 to 100 r.p.m. stirring speed. The forming of toner size particles at slow speeds by utilizing large amounts of suspending agents creates difficulties as set forth above as suspending agents in large amounts must be removed from the particles in order for them to operate effectively as toner particles. The conventional reactors with paddle blade stirrers when operating at high speeds produce a broad range of particle sizes.

As can be seen, there remains a need for a process of producing toners which would not involve extensive processing steps of polymer formation, colorant addition, mixing and particle formation. There remains a need for a process which would produce toner particles directly from monomer that have good triboelectric properties, abrasive resistance, blocking resistance, narrow size variation, and good colorant loading capability. Since the prior forming methods are deficient in one or more of the above areas, there is a continuing need for an improved method of formation of toners for use in electrophotographic development.

According to the present invention, there is provided a method of toner formation comprising dispersing pigment in monomer, subjecting the pigment-containing monomer to high shear treatment in an aqueous medium to form toner-sized, pigment-containing monomer particles in suspension, agitating the suspension during polymerization of the monomer, and recovering toner particles.

In accordance with the invention it has been found that the pigmented monomer particles obtained after initial suspension and sizing can be stable such that they may be transferred to a reactor and stirred at relatively low speeds of between 75 and 100

r.p.m. and can remain in suspension during polymerization to form toner.

In order that the invention may be more fully understood, some embodiments in accordance therewith will now be described with reference to the accompanying drawings, wherein:—

Figure 1 is a view of a rotor stator mixer.

Figure 2 is a view of the static element of a rotor stator mixer.

Figure 3 is a view of the rotating element of the mixer.

Figure 4 illustrates a base construction for a rotor stator mixer.

The toner formation process of the invention is carried out in one instance by the use of a styrene monomer to which is added lauroyl peroxide and Molacco-H carbon black that has been treated with an active silane dispersion agent such as triethoxy silane ("Siliclad"), a reactive silane. The carbon particles are coated with the silane by suspension of the carbon in water followed by the addition of the triethoxy silane ("Siliclad", Clay Adams Division of Becton Dickinson Co.). The mixture of silane and carbon is agitated to allow the silane to form a coat on the surface of the carbon particles. The treated (cladded) carbon is dispersed in a styrene monomer with lauroyl peroxide. Then, utilizing a short period of mixing in a high speed and high shear mixer, the monomer is suspended in an aqueous medium and toner size particles are formed. The suspension of toner size pigmented monomer is then transferred to a reactor which is agitated by a stirrer at about 75 r.p.m. as polymerization takes place. After polymerization is complete, the particles are recovered and found to be suitable for use as toner materials without further processing.

Any polymeric material which may be formed by dispersion polymerization and which has a melting point within the range suitable for use as a toner may be used in the toner forming process of the present invention. Typical monomeric units which may be employed to form polymers include: styrene, p-chlorostyrene; vinyl naphthalene; ethylenically unsaturated mono-olefins such as ethylene, propylene, butylene, isobutylene and the like; vinyl halides such as vinyl chloride, vinyl bromide, vinyl fluoride and the like; vinyl esters such as vinyl acetate, vinyl propionate, vinyl benzoate, vinyl butyrate and the like; esters of aliphatic monocarboxylic acids such as methyl acrylate, ethyl acrylate, n-butylacrylate, isobutyl acrylate, dodecyl acrylate, n-octyl acrylate, 2-chloroethyl acrylate, phenyl acrylate, methyl-alpha-chloroacrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate and the like; acrylonitrile, methacrylonitrile, vinyl ethers such as vinyl methyl ether, vinyl isobutyl ether, vinyl ethyl ether, and the like; vinyl ketones such as vinyl methyl ketone, vinyl hexyl ketone, methyl isopropenyl ketone and the like; vinylidene halides such as vinylidene chloride, vinylidene chlorofluoride and the like; and N-vinyl compounds such as N-vinyl pyrrole, N-vinyl carbazole, N-vinyl indole, N-vinyl pyrrolidone and the like; and mixtures thereof. The styrene resins may also be formed by the polymerization of mixtures of two or more of these unsaturated monomeric materials with a styrene monomer. The expression "addition polymerization" is intended to include known polymerization techniques, such as radical, anionic and cationic polymerization processes. Monomers forming polystyrene and copolymers of

vinyl methyl ether, vinyl isobutyl ether, vinyl ethyl ether, and the like; vinyl ketones such as vinyl methyl ketone, vinyl hexyl ketone, methyl isopropenyl ketone and the like; vinylidene halides such as vinylidene chloride, vinylidene chlorofluoride and the like; and N-vinyl compounds such as N-vinyl pyrrole, N-vinyl carbazole, N-vinyl indole, N-vinyl pyrrolidone and the like; and mixtures thereof. Generally, suitable vinyl resins employed in the toner have a weight average molecular weight of from 3,000 to about 500,000.

Toner resins containing a relatively high percentage of styrene resins are typically preferred. The presence of a styrene resin is preferred because a greater degree of image definition is achieved with a given quantity of additive material. Further, denser images are obtained when at least about 25 percent by weight, based on the total weight of resin in the toner, of a styrene resin is present in the toner. The styrene resin may be a homopolymer of styrene or styrene homologues or one or more copolymers of styrene with other monomeric groups containing a single methylene group attached to a carbon atom by a double bond. Thus, typical monomeric materials which may be copolymerized with styrene by addition polymerization include: p-chlorostyrene; vinyl naphthalene; ethylenically unsaturated mono-olefins such as ethylene, propylene, butylene, isobutylene and the like; vinyl halides such as vinyl chloride, vinyl bromide, vinyl fluoride and the like; vinyl esters such as vinyl acetate, vinyl propionate, vinyl benzoate, vinyl butyrate and the like; esters of alpha-methalene aliphatic monocarboxylic acids such as methyl acrylate, ethyl acrylate, n-butylacrylate, isobutyl acrylate, dodecyl acrylate, n-octyl acrylate, 2-chloroethyl acrylate, phenyl acrylate, methyl-alpha-chloroacrylate, methyl methacrylate, ethyl methacrylate butyl methacrylate and the like; acrylonitrile, methacrylonitrile, acrylamide, vinyl ethers such as vinyl methyl ether, vinyl isobutyl ether, vinyl ethyl ether, and the like; vinyl ketones such as vinyl methyl ketone, vinyl hexyl ketone, methyl isopropenyl ketone and the like; vinylidene halides such as vinylidene chloride, vinylidene chlorofluoride and the like; and N-vinyl compounds such as N-vinyl pyrrole, N-vinyl carbazole, N-vinyl indole, N-vinyl pyrrolidone and the like; and mixtures thereof. The styrene resins may also be formed by the polymerization of mixtures of two or more of these unsaturated monomeric materials with a styrene monomer. The expression "addition polymerization" is intended to include known polymerization techniques, such as radical, anionic and cationic polymerization processes. Monomers forming polystyrene and copolymers of

styrene and n-butylmethacrylate have been found to be particularly suitable for the polymerization process of the invention as they result in good yields of completely polymerized monomer which are suitable for use as toner material as they possess good triboelectric and fusing properties.

Any suitable pigment material may be used in the process of the invention. A pigment generally should be capable of being dispersed in a monomer, be insoluble in the water used in the cladding and polymerization processes and give strong, clear, permanent colors when used as toner. Typical of such pigments are phthalocyanines, lithols, toluidene and inorganic pigments such as TiO_2 and dyes. Typical of phthalocyanine pigments are copper phthalocyanine, mono-chlor copper phthalocyanine, hexadecachlor copper phthalocyanine, metal-free phthalocyanine, mono-chlor metal free phthalocyanine, and hexadecachlor metal-free phthalocyanines; athraquinone vat pigments such as: vat yellow 6 GL CI 1127, quinone yellow 18-1, idanthrone CI 1106, pyranthrones CI 1096; brominated pyranthrones such as: dibromopyranthrene, vat brilliant orange RK, anthrimide brown CI 1151, dibenzanthrone green CI 1101, flavanthrone yellow CI 1118; thioindigo pigments such as: thioindigo red and pink FF; azo pigments such as: toluidine red CI 69 and hanza yellow; and metalized pigments such as: azo yellow (green gold) and permanent red. Carbon black has been found to be a preferred colorant as it is low in cost, may be completely cladded so as not to inhibit polymerization, and provides strong black images at relatively low loading of the colorant. The carbon black may be of any of the known types such as channel black or furnace black. The furnace black is preferred as it is lower in cost. The amount of carbon black necessary in the toner typically is between 1 and 20 percent. A loading of between 5 and 10 percent in the toner has been found to be suitable for the process of the invention.

If necessary, a reactive material which allows the coating (cladding) of the pigments to prevent their inhibition of or reaction with the monomer during its polymerization may be used in the invention. Coating is not necessary in the case of most dyes and inorganic pigments. Typical of such cladding materials are water soluble monomers that precipitate onto carbon black or other pigments such as neutralized poly-acrylic acid and reactive silanes such as amine silicate-organosilane copolymers. Acrylonitrile monomer has been found to be a suitable water soluble monomer which will precipitate onto carbon. The reactive silanes of water emulsified or water soluble types have been found to be suitable for the cladding process. Typical of suitable silanes are those

having functional groups selected from: amino, methacrylate, epoxide, polyamino, mercapto, vinyl, chloroalkyl, and alkoxy; typical of suitable alkoxy silanes are methyltrimethoxysilane, phenyltrimethoxysilane, methylphenyldimethoxysilane, diphenyldimethoxysilane. Siloxanes may also be employed; typical of suitable siloxanes is hexamethyldisiloxane. A preferred silane is a triethoxy silane [$C_{18}H_{37}-Si(C_2H_5O_3)$] marketed as "Siliclad" by the Clay Adams Division of Becton, Dickinson and Company, which gives a good polymeric coating on carbon black that prevents hydrophilic and other types of reaction. A system containing cladded carbon will polymerize in about the same time as one not containing carbon.

The cladding agent when utilized is provided in any amount which provides a covering of the pigment sufficient to prevent the pigment inhibiting complete polymerization to form the toner. Generally, the cladding agent is used in an amount that is the minimum which will give complete coverage as this keeps the expense and time of cladding low. Typically, an amount of cladding agent from 0.05 to 10 percent by weight of the pigment may be utilized. A suitable range has been found to be 0.1 to 4 percent by weight of the pigment. A preferred range in the case of triethoxy silane is from 1 percent to 3 percent for complete coverage at low cost.

Methods of forming a toner by a suspension polymerisation technique employing pigment cladding procedures such as outlined above are described and claimed in our co-pending Patent Application No. 32193/77 (Serial No. 1,583,411)

Any initiator which is compatible with the particular monomer being used may be utilized in the process of the invention. Typical of initiators for polymerization are the peroxide and azo initiators. Among those found suitable for use in the process of the invention are azobis(2-methylproprionitrile) and lauroyl peroxide which result in complete polymerization without leaving detrimental residual materials or requiring high temperatures or pressures.

The initiator may be added to the monomer during dispersion of the carbon black or other pigment or may be mixed in after the carbon black dispersion. It is preferred that the polymerization initiator, treated carbon black or other pigment and monomer be mixed in high shear agitation to produce a stable dispersion of the pigment in the monomer. The carbon or other pigment in stable dispersion is separated into sub-micron size particles evenly distributed throughout the monomer. The mixture may be heated during dispersion. Generally, the initiator is used in the amount necessary to achieve complete polymerization without

waste of the initiator. An amount of between 2 percent and 10 percent by weight initiator to monomer has been found to be generally suitable. A preferred range is 2 to 5 percent by weight of initiator to monomer to give complete polymerization without waste at low cost. The optimum amount in the instance of lauroyl peroxide with styrene monomer systems is about 2 percent as this gives complete polymerization at low cost and results in good toner properties.

Any suitable carrier may be used with the toner of the present invention to form a developer. Suitable coated and uncoated carrier materials for cascade and magnetic brush development are well known in the art. The carrier particles may be electrically conductive, insulating, magnetic or nonmagnetic provided that the carrier particles acquire a charge having an opposite polarity to that of the toner particles when brought in close contact with the toner particles so that the toner particles adhere to and surround the carrier particles. When a positive reproduction of an electrostatic image is desired, the carrier particle is selected so that the toner particles acquire a charge having a polarity opposite to that of the electrostatic latent image. Alternatively, if a reversal reproduction of the electrostatic image is desired, the carriers are selected so that the toner particles acquire a charge having the same polarity as that of the electrostatic image. Thus, the materials for the carrier particles are selected in accordance with their triboelectric properties in respect to the electroscopic toner so that when mixed or brought into mutual contact, one component of the developer is charged positively if the other component is below the first component in the triboelectric series and negatively if the other component is above the first component in the triboelectric series. By proper selection of materials in accordance with their triboelectric effects, the polarities of their charge when mixed are such that the electroscopic toner particles adhere to and are coated on the surfaces of carrier particles and also adhere to that portion of the electrostatic image bearing surfaces having a greater attraction for the toner than do the carrier particles. Typical carriers include sodium chloride, ammonium chloride, aluminum potassium chloride, Rochelle salt, sodium nitrate, aluminum nitrate, potassium chlorate, granular zircon, granular silicon, polymethyl methacrylate, glass, steel, nickel, iron, ferrites, ferromagnetic materials and silicon dioxide. 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 No. 2,618,551; L. E. Walkup et al in U.S. Patent No. 2,638,416; E. N. Wise in U.S. Patent No. 2,618,552; R. J. Hagenbach et al in U.S. Patent No. 3,591,503 and U.S. Patent No. 3,533,835; and B. J. Jacknow et al in U.S. Patent No. 3,526,533. Suitable carriers for use with the toners of the present invention include nickel berry, coated ferrites and methyl terpolymer coated steel. Nickel berry is a nodular nickel particle disclosed in U.S. Patent No. 3,767,568 having a pebbled surface. Methyl terpolymer coated steel carrier is a steel core coated with a composition such as that of Example XIII of U.S. Patent No. 3,526,533. An ultimate coated carrier particle diameter between 50 microns and 1,000 microns is generally suitable because the carrier particles then possess sufficient density and inertia to avoid adherence to the electrostatic images during the cascade development process. A range of 75 to 400 microns is generally preferred to give clear, sharp images. 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 No. 3,186,838. Also, print deletion occurs when carrier beads adhere to electrostatographic imaging surfaces.

It is generally desirable to utilize a stabilization agent other than the monomer itself in the solution. Such an agent aids the formation of particles which will remain dispersed in the water during polymerization. The stabilization agent stabilizes the particles so they remain dispersed and do not agglomerate during polymerization. Polymers pass through tacky stages when they have a strong tendency to agglomerate during polymerization. Any suitable stabilization agent may be used. Typical of such stabilizers are both non-ionic and ionic water soluble polymeric stabilizers such as methyl cellulose, ethyl cellulose, sodium salt of carboxyl methyl cellulose, polyacrylate acids and their salts, polyvinyl alcohol, gelatins, starches, gums, alginates, zein and casein. Suitable stabilization agents are polyacrylic acid, polymethacrylic acid, polyacrylamide and polyethylene oxide. Stabilizing agents found to be preferred for this invention are polyethylene oxide—polypropylene block copolymers and polyvinyl alcohols, which give good suspension at low concentration and narrow particle range. The stabilizer is generally added in a ratio based on the amount of water. An amount of between 0.2 and 5 percent by weight stabilizer to water is generally suitable. An amount of between 0.2 and 1.5 percent is preferred to give good suspension at low cost and low impurity in the toner. An optimum amount for use in formation of toners is between 0.75 and 1

percent to give low materials cost and narrow size distribution. The preferred polyvinyl alcohol contains from 1 to 20 mole percent of polyvinyl acetate groups. The optimum amount of polyvinyl acetate is about 16 mole percent to give good dispersion at low concentration and narrow particle size range. The molecular weight of suitable polyvinyl alcohols is between 10,000 and 125,000 number average molecular weight. A preferred polyvinyl alcohol is Monsanto 20-60 of about 90,000 weight average molecular weight. The preferred polyethylene oxide-polypropylene (PEO-PPO) block copolymers comprise 40 to 80 weight percent ethylene oxide. Suitable molecular weights of the (PEO-PPO) block copolymer are between 3,000 and 27,000 weight average molecular weight. A preferred range of molecular weight is between 10,000 and 15,000 weight average to give good dispersion at low concentration.

The dispersing of pigment-containing monomer may be carried out in any suitable type of mixer which results in toner particles of narrow size distribution in stable suspension in less than about 3 minutes. The mixer may be of either the batch or in-line type. Suitable for the process of the invention are reed type ultrasonic mixers such as the Dispersionic (registered Trade Mark) mixers. A preferred type mixer for the process is the rotor stator type mixer such as the Polytron (registered Trade Mark) or Dispac in which one element is stationary and the other rotates in close tolerance therewith while the liquid is drawn through apertures in the static element. The shear rate should be greater than 10^3 sec^{-1} . An axial turbine agitator that comprises an arrangement of discs and paddles is the other preferred type of mixer. The axial turbine mixers are found to form stable dispersions of narrow particle size distribution at speed ranges of 200 to 3,000 r.p.m.

The drawings illustrate a preferred type of rotor stator mixer. The mixer comprises a static element 22 as shown in Figure 2. The static element comprises raised elements 15 separated by slots having a bottom 12. The static element is mounted on base 21 supported by mounting element 24. Gaskets such as 23 are used in mounting of the element. Figure 3 illustrates the rotating element 31 of the mixer. The rotating element has blades 34 which correspond in height to the depth of the slots in the static element. The rotor is provided with a base 32 having an indented portion 33 for attachment to suitable drive means, not shown, such as a high speed blender. Figure 1 illustrates the rotor and static element assembled to the mixing unit 11. The rotor is in close clearance with the static element and rotates around center 14. Figure 4 illustrates attach-

ment means for the mixer wherein a collar 42 is placed over base 24 of static element 22. The static element is secured with nut 43, keyed washer 44 and rubber shim 45. The indented portions of the rotor allow better flow of the material being treated.

The shear applied by the sizing mixer is the amount which results in narrow size range distribution. The preferred rotor stator mixer applies a high shear mixing of greater than 10^3 sec^{-1} for 10 seconds to 2 minutes to achieve a size range between 2 and 30 microns with about 95 percent between 5 and 20 microns. The volume average particle size is 12 to 13 microns.

The time of high shear mixing in part varies with the viscosity of the aqueous medium in which the pigmented monomer is suspended. Generally, the stabilization agent changes the viscosity of the aqueous suspension medium. A suitable viscosity range generally is between 1 and 100 centipoises (cps). The preferred viscosity of the aqueous suspension medium is between 1 and 10 centipoises (cps) to give low cost and rapid mixing. An optimum range is 1 to 3 cps to give a stable dispersion of monomer with short mixing time, low cost and little impurity in the toner.

The rotor stator high speed high shear mixer is capable of producing narrow toner particle ranges. The size range of particles is affected by the viscosity of the aqueous solution, viscosity of the monomer and ratio of monomer to aqueous suspending medium. A suitable mixture is when the pigment containing monomer forms from 0.2 to 40 percent of the total volume of the monomer and water mixture. The size range produced may suitably be between 2 and 30 microns, preferably between 5 and 30 microns. However, for best toner performance, it is preferred that at least 95% of the particles be between 5 and 20 microns.

In accordance with a preferred procedure, the high shear treatment is conducted in a first vessel and the step of agitating the suspension is conducted in a second vessel after transfer. Preferably the particles transferred from the first vessel have sizes in the range from 15 microns to 25 microns.

In the method of the invention, the agitation of the suspension is preferable carried out for longer than 3 hours; for example, in one preferred procedure polymerization is complete in about 6 hours.

The following Examples further define, describe, and compare methods of preparing developers of the present invention and of utilizing them in electrophotographic applications. Parts and percentages are by weight unless otherwise indicated.

EXAMPLE I

To 100 grams of styrene are added 5 130

grams of lauroyl peroxide which are mixed until dissolved. To this mixture is added 7 grams of a cladded carbon black, Molacco-H ("Molacco" is a registered Trade Mark), which has been treated with triethoxy silane, Siliclad, in an about 2 percent solution with water in a stirred beaker for about 5 minutes to prevent interference with the polymerization. This mixture is heated with mixing in a Waring Blender to about 70°C for about 5 minutes to provide a good dispersion of carbon black in the monomer mix. The pigmented monomer mix is then poured into a Waring Blender jar equipped with a Polytron mixing head along with about 500 cc of about 1.25 percent polyvinyl alcohol-water solution. The two phase mixture is then stirred at about 3,000 r.p.m. for about 30 seconds to produce a pigmented droplet dispersion with an average size of about 12 microns.

The sized dispersion is transferred to a reactor vessel consisting of a 1,000 ml. round bottomed flask equipped with a paddle blade stirrer. With stirring speed of 60 to 80 r.p.m. the flask is heated to about 70°C and controlled at that temperature by means of a constant temperature water bath.

The progress of the polymerization is followed by injecting samples at various time intervals into a gel permeation chromatograph. The rate of disappearance of both monomer and catalyst is thus determined. After six hours, the polymerization is complete and the suspension of 12 micron sized pigmented particles is poured into three liters of cold water. The resulting diluted suspension is centrifuged 15 minutes at 1,000 r.p.m. in a bucket type centrifuge. The supernatant liquid consisting of the diluted polyvinyl alcohol is decanted, fresh water is added and the mixture is shaken for 5 minutes to disperse the particles. This washing procedure is repeated three times. After the final wash, the sedimented slurry is poured into a stainless steel tray and allowed to air dry. The resulting cake is very friable and can be broken down to individual particles by tumbling on a roll mill. The particles have an average particle size between 8 and 12 microns. The divided particles are utilized in a Model D processor and found to produce good images.

55 EXAMPLE II

100 parts monomer consisting of a 65:35 ratio of styrene and n-butyl methacrylate, 10 parts carbon black treated as in Example I, 1 part ethyl cellulose, 2 parts azobisisobutyronitrile were mixed in a Waring Blender to give a well dispersed carbon black. This mixture was added to 500 parts of 0.5 percent polyvinyl alcohol solution in a Waring Blender jar equipped with a Polytron mixing head. The mixture was agitated at

about 3,000 r.p.m. for 30 seconds to disperse the pigmented monomer phase in the water phase. The resulting dispersion was further stabilized by the addition of sufficient 5 percent polyvinyl alcohol solution to yield a 2.6 percent concentration of polyvinyl alcohol. The stabilized dispersion was then transferred to a 1,000 ml. polymerization flask equipped with an argon purge and paddle stirrer, and heated to 65° C while stirring at 60 r.p.m. After eight hours, the resulting polymer dispersion was cooled by pouring into three liters of cold water. The particles were recovered by sedimentation and consisted of uniformly black spheres with an average particle diameter of 10 microns. These particles utilized in a Model D processor produce images of good quality.

85 EXAMPLE III

The process of Example I is repeated except that TiO₂ is substituted for the carbon black and is not cladded. The particles formed exhibit good xerographic properties and are completely polymerized. The particles are operable in a xerographic reproduction process utilizing a Model D processor and have a size between 5 and 15 microns.

100 EXAMPLE IV

The process of Example I is repeated except that Dow Corning reactive silane DC-Z-6020 is substituted for the Siliclad. This is found to produce toner which has good xerographic properties.

105 EXAMPLE V

The process of Example II runs 7 and 8 of British Patent 1,319,815, which is hereby incorporated by reference, is performed utilizing Molacco-H carbon black which has been cladded in accordance with the process of Example I of the present specification in place of the No. 35 Asahi Carbon of the patent. Further, dispersion is carried out first in a high speed blender of Example I, then by slow speed agitation. The toner recovered is found to be completely polymerized, exhibits good copying qualities and is not subject to blocking. Further, the size range is such that 95 percent of the particles are between 5 and 20 microns.

120 EXAMPLE VI

The process of Example I was performed except that an axial turbine agitator at 2,000 r.p.m. is substituted for the rotor stator (Polytron) mixer. The particles that result have a particle range of about 95 percent between 5 and 30 microns. The particles are operable as toner when utilized in a Model D processor.

EXAMPLE VII

As a control, the process of Example I is performed with particle sizing taking place by high speed stirring of the paddle blade stirrer at about 1,000 r.p.m. for about 15 minutes. The paddle stirrer is then slowed to about 75 r.p.m. for completion of polymerization. The particles recovered have a size range of about 95 percent between 5 and 100 microns and are operable as toner.

EXAMPLE VIII

The process of Example I is performed utilizing acrylonitrile monomer in an amount of about 1.7 percent with water as the cladding agent. The toner produced is of good quality.

EXAMPLE IX

The process of Example I is repeated except that 2.5 percent by weight acrylonitrile monomer is substituted for the triethoxy silane. The toner has good triboelectric properties, is not subject to blocking and is completely polymerized.

EXAMPLE X

The process of Example II is repeated except about 3 percent by weight of hexamethyldisiloxane is substituted for the triethoxy silane. The toner is completely polymerized and has good triboelectric properties. The particles have a particle size of about 95 percent between 5 and 20 microns.

EXAMPLE XI

As a control, the process of Example I is repeated except the dispersion of treated carbon black and monomer is transferred directly into the reactor vessel. The reactor vessel contains about 600 cc of a 1.5 percent by weight solution of Pluronic F-127 a 70/30 polyethylene oxide—polypropylene block copolymer; "Pluronic" is a registered Trade Mark. The paddle is rotated at about 800 r.p.m. for 5 minutes and then slowed to about 85 r.p.m. for polymerization. The particles have a size range of about 95 percent of the particles between 5 to 85 microns. The particles develop good images when used in a Model D processor. The particles are completely polymerized. This illustrates the wider particle range obtained without the high shear, high speed mixing step.

EXAMPLE XII

The process of Example I is repeated substituting Monsanto 2060 a polyvinyl alcohol of about 90,000 weight average molecular weight having about 16 mole percent polyvinyl acetate groups for the polyvinyl alcohol of Example I. The toner exhibits excellent xerographic properties and

has about 95 percent of the particles between 5 and 25 microns.

EXAMPLE XIII

The process of Example I is repeated except that about 2 percent methyltrimethoxysilane is substituted for the reactive silane of Example I. The particles are found to be completely polymerized, satisfactory in xerographic properties and of a size range of about 95 percent between 5 and 20 microns.

EXAMPLES XIV—XV

The processes of Examples I and II are repeated substituting about 1 percent by weight diphenyldimethoxy silane for the reactive silanes of Examples I and II. The toners produced have good properties and are completely polymerized. The particles have a size range of about 95 percent between 5 and 20 microns.

Although specific materials and conditions were set forth in the above examples of processes for the formation of the toner of the invention, these are merely intended as illustrations of the present invention. Various other substituents and processes such as those listed above, may be substituted for those in the Examples with similar results. Further steps may be added to those used to prepare the toner of the present invention. In addition, other materials may be incorporated into the toner of the invention which will enhance, synergize or otherwise desirably effect the properties of these materials for their present use. For example, additives to increase resistance to moisture absorption or to affect triboelectric properties, could be added to the surface of the particles.

Other modifications of the present invention will occur to those skilled in the art upon a reading of the present disclosure. For instance, magnetic pigments could be used in the process if it was desired that magnetic toner be produced. Further, if toner for use in developing processes other than magnetic or cascade were desired, the particle size could be regulated to be smaller such as 1 to 5 microns for use in powder cloud development processes. Further the sizing may be performed as a thru-put or in line process rather than the batch process illustrated.

If desired, any suitable chain transfer agents or cross-linking agent may be used in the invention to modify the polymeric toner to produce particularly desired properties. Typical of crosslinking agents which may be used in the invention are aromatic divinyl compounds such as divinylbenzene, divinyl naphthalene or derivatives thereof; diethylenecarboxylate esters such as diethyleneglycol methacrylate, diethyleneglycol

acrylate; any other divinyl compounds such as divinyl sulfide or divinyl sulfone compounds provided with three or more vinyl radicals; or mixtures of the foregoing compounds. Chain transfer agents act to control molecular weight by inhibiting chain growth. Typical of chain transfer agents which may be used in the method of the invention are mercaptans such as laurylmercaptan, phenylmercaptan, butylmercaptan, dodecylmercaptan; or halogenated carbons such as carbon tetrachloride or carbon tetrabromide. Also, examples of materials which become effective when used in a much larger amount such as solvents for the vinyl monomer are substituted aromatic compounds such as toluene or isopropylbenzene; or substituted fatty acids such as trichloroacetic acid or tribromoacetic acid. Also, examples of materials which can be added as a monomer to be incorporated in the resulting polymer and simultaneously effect molecular weight control are ethylenic unsaturated monoolefins with radicals such as propylene or isobutylene; allyl compounds such as allyl benzene, allyl acetate or allylidene chloride.

WHAT WE CLAIM IS:—

1. A method of toner formation comprising dispersing pigment in monomer, subjecting the pigment-containing monomer to high shear treatment in an aqueous medium to form toner-sized, pigment-containing monomer particles in suspension, agitating the suspension during polymerization of the monomer, and recovering toner particles.

2. A method according to claim 1 wherein said pigment is carbon black.

3. A method according to claim 1 or claim 2 wherein said monomer further comprises a material selected from crosslinking agents, chain transfer agents and mixtures thereof.

4. A method according to any one of claims 1 to 3 wherein said monomer comprises styrene.

5. A method according to any one of claims 1 to 4 wherein the agitation of the suspension is carried out for longer than 3 hours.

6. A method according to any one of claims 1 to 5 wherein said toner particles range in size from 2 to 30 microns.

7. A method according to any one of claims 1 to 6 wherein at least 95 percent of said particles are between 5 and 20 microns.

8. A method according to any one of claims 1 to 7 wherein said pigment-containing monomer forms 0.2 to 40 percent of the total volume of the monomer and water mixture.

9. A method according to any one of claims 1 to 8 wherein an initiator is present during the step of dispersing pigment in monomer.

10. A method according to claim 9 wherein said initiator is present in an amount between 2 percent and 10 percent by weight of said monomer.

11. A method according to claim 9 or claim 10 wherein said initiator is lauroyl peroxide.

12. A method according to any one of claims 1 to 11 wherein an effective amount of stabilizer is present during said high shear treatment.

13. A method according to claim 12 wherein said stabilizer is polyvinyl alcohol.

14. A method according to claim 12 wherein said stabilizer comprises a material selected from polyethylene oxide, polyacrylic acid, polymethacrylic acid, polyacrylamide and mixtures thereof.

15. A method according to any one of claims 12 to 14 wherein said stabilizer is present in an amount between 0.2 and 5 percent by weight of said aqueous medium.

16. A method according to claim 12 wherein said stabilizer is present in an amount between 0.75 and 1 percent by weight of the water.

17. A method according to any one of claims 1 to 16 wherein the high shear treatment is carried out for from 10 seconds to 2 minutes.

18. A method according to any one of claims 1 to 17 wherein said toner particles are spherical.

19. A method according to any one of claims 1 to 18 wherein said high shear comprises a greater than 10^3 sec^{-1} shear rate.

20. A method according to any one of claims 1 to 19 wherein said pigment, said monomer and a polymerization initiator are subjected to high shear mixing for the step of dispersing pigment in monomer.

21. A method according to any one of claims 1 to 20 wherein heat is applied during the step of dispersing pigment in monomer.

22. A method according to any one of claims 1 to 21 wherein heat is applied to aid in initiating and carrying out said polymerization.

23. A method according to any one of claims 1 to 22 wherein polymerization is complete in about 6 hours.

24. A method according to any one of claims 1 to 23 wherein said pigment is treated prior to dispersion in monomer by a method comprising suspension of the pigment in a solution of water and a water-soluble monomer.

25. A method according to claim 24 wherein said monomer comprises a silane or siloxane.

26. A method according to claim 25 wherein said monomer is a silane having a functional group or groups selected from: amino, methacrylate, epoxide, polyamino, mercapto, vinyl, chloroalkyl and alkoxy.

27. A method according to claim 24 wherein said monomer comprises acrylonitrile monomer. 30
- 5 28. A method according to any one of claims 24 to 27 wherein the step of treating the pigment comprises forming a coating on the pigment. 30
- 10 29. A method according to any one of claims 24 to 28 wherein said monomer is present in an amount of 0.1 to 4 percent by weight of the pigment. 35
- 15 30. A method according to any one of claims 1 to 29 wherein said high shear mixing utilizes an axial turbine mixer. 40
- 20 31. A method according to any one of claims 1 to 29 wherein said high shear treatment utilizes a rotor stator type mixer. 45
- 25 32. A method according to any one of claims 1 to 31 wherein the viscosity of said aqueous medium is between 1 and 100 centipoises. 50
33. A method according to any one of claims 1 to 32 wherein the viscosity of said aqueous medium is between 1 and 10 centipoises.
34. A method according to any one of claims 1 to 33 wherein the high shear treatment is conducted in a first vessel and the step of agitating the suspension is conducted in a second vessel after transfer.
35. A method according to claim 34 wherein the particles transferred from the first vessel have sizes in the range from 15 microns to 25 microns.
36. A toner whenever produced by a method in accordance with any one of claims 1 to 35.
37. A xerographic developer comprising a toner in accordance with claim 36.
38. A xerographic developer comprising xerographic carrier particles and a toner in accordance with claim 36 electroscopically carried by said carrier particles.
39. A method of developing an electrostatic latent image, comprising treating the latent image with a developer in accordance with claim 37 or claim 38 so that toner particles are electrostatically deposited on said latent image so as to form a corresponding visible image.

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FIG. 1

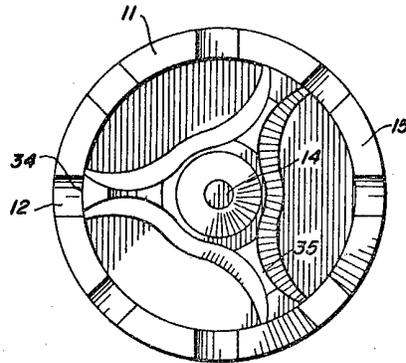


FIG. 2

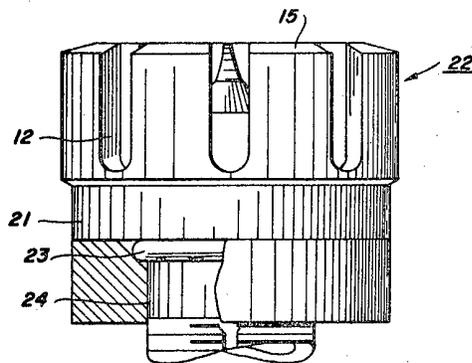


FIG. 3

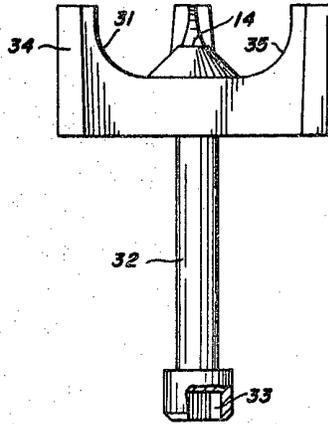


FIG. 4

