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(54) Magnetic colored encapsulated toner compositions.

(57) An encapsulated toner composition comprised of a core comprised of a polymer resin, color pigment, dye or mixtures thereof, a substantially colorless magnetic material, and a whitening agent; which core is encapsulated in a polymeric shell.

Rank Xerox (UK) Business Services

BACKGROUND OF THE INVENTION

The present invention is generally directed to toner compositions, and more specifically to colored encapsulated toner compositions. In one embodiment, the present invention is related to magnetic colored encapsulated toner compositions comprised of a core and a polymeric shell thereover preferably prepared by interfacial polymerization, which shell may contain a silane component derived from the reaction of organosilane reagents such as a functionalized alkoxysilane, a siloxysilane, and the like, with shell precursor materials. An embodiment of the present invention relates to conductive colored, other than black, encapsulated toner compositions suitable for inductive single component development with no carrier component, which toner composition is comprised of a core comprised of a suitable polymer resin, a colorless or lightly colored such as grayish light orange, or a light brown magnetic material, such as iron powders, iron oxides, surface treated or surface coated magnetic pigments, finely divided magnetic particles dispersed in polymeric and the like, a whitening agent, and dye or pigment particles, which core is encapsulated by a polymeric shell, such as a polyurea, polyurethane, polyamide, polyester, mixtures thereof, and the like, and which shell also has incorporated therein, or thereon a layer of a conductive component. The core resin for the encapsulated toners of the present invention may also contain a siloxane or polysiloxane moiety to enhance its release property. In an embodiment of the present invention there can be selected for the magnetic material a grayish colored iron powder, Sicopur 4068 available from BASF, which iron powder it is believed has a high saturation magnetic moment of over 90 emu per gram. In another embodiment of the present invention, there is provided a colored single component encapsulated toner composition comprising a core comprised of, for example, a methacrylate polymer resin or the copolymers thereof, a colorant, such as cyan, magenta, yellow, or other colored pigments or dyes, mixtures thereof, and the like, Sicopur 4068 iron powder, and a whitener such as titanium dioxide or tin dioxide powder; and wherein the aforementioned core is encapsulated in a polymeric shell, and which shell can be coated with a layer of conductive agents. In an embodiment of the present invention, there are provided single component magnetic colored encapsulated toner compositions comprised of a polymeric shell obtained by interfacial polymerization, and a core comprised of polymers obtained preferably by free radical polymerization, colorants, an iron powder or other colorless or lightly colored magnetic material with a particle size diameter of from about 0.1 to about 8 microns, and a whitener comprised of a white inorganic pigment such as titanium dixoide, tin dixoide or other whitening agents, and wherein the toner surface is coated, for example, by dry blending process with a conductive powder. In another embodiment, the present invention relates to a magnetic colored encapsulated toner composition without the aforementioned surface conductive layer, which toner composition is especially useful for xerographic process wherein image toning and transfer are accomplished electrostatically, and the fixing of the image on paper is achieved in a separate step with a pressure roll. Examples of advantages associated with many of the toner compositions of the present invention include excellent color quality and color variety, improved toner fixing characteristics, suitability for use in the ionographic imaging systems, such as Delphax S6000TM, S4500TM, S3000TM and Xerox Corporation 4075TM, which employ inductive single component development systems, suitability for highlight color imaging processes, the elimination or the minimization of image ghosting, superior release properties enabling their selection, for example, in imaging systems wherein a release fluid, such as a silicone oil, is avoided, no or minimal toner agglomeration, excellent powder flow characteristics, no or minimal leaching of the core components, and avoidance of core resin component adherence to, for example, dielectric receivers or photoreceptors. The toner compositions of the present invention can be selected for a variety of known reprographic imaging processes including electrophotographic and ionographic processes. In an embodiment, the toner compositions are selected for pressure fixing processes wherein the image is fixed onto paper with pressure. Pressure fixing is utilized in some reprographic imaging processes. In some ionographic processes, latent images are first generated on a dielectric receiver such as silicon carbide, reference U.S. Patent 4,885,220, the disclosure of which is totally incorporated herein by reference. The latent images are toned with a conductive toner by inductive single component development, and transferred and fixed simultaneously (transfix) in one single step onto paper with pressure. Specifically, the toner compositions of the present invention can be selected for known inductive single component developmet processes, such as those utilized in the Delphax based ionographic printers. This printing process involves the generation of latent images on a dielectric receiver with an ion deposition head, toning the images with a conductive toner encapsulated toner of the present invention by inductive development, and transfixing to paper with an applied pressure of, for example, from about 1,000 to about 5,000 psi. The toner of the present invention can be selected for the generation of colored images in the commercial Delphax printers such as the Delphax S9000TM, S6000TM, S4500TM, S3000TM, and Xerox Corporation printers such as the 4060TM and 4075TM wherein, for example, transfixing is utilized. The toner compositions of the present invention are particularly useful for highlight colored imaging processes as indicated herein. In another embodiment of the present invention, the toner compositions of the present invention can be rendered insulative without the application of a surface conductive coating, and can thus, for example, be utilized in xerographic imaging and printing apparatuses wherein image toning and transfer are accomplished electrostatically, and transferred images are fixed in a separate step by means of a pressure roll with or without the assistance of thermal energy fusing.

The toner compositions of the present invention can, in one specific embodiment, be prepared by a number of methods including first dispersing the toner precursor materials into stabilized microdroplets of controlled droplet size and size distribution, followed by shell formation around the microdroplets via interfacial polymerization, and subsequently generating the core polymer resin by in situ addition polymerization, preferably free radical polymerization within the newly formed microcapsules. The encapsulated particles thus obtained can be washed, dried, and surface treated with conductive additives by dry blending process to impart to the particles the required conductivity characteristics. In one embodiment, the present invention is directed to a process for the simple, and economical preparation of pressure fixable magnetic colored encapsulated toner compositions by interfacial/free radical polymerization methods wherein there are selected as the core polymer resin precursors an addition-type monomer or monomers, a colored, other than black, pigment or dye, a colorless or lightly colored magnetic material of high magnetic saturation moment, a whitening agent, shell-forming monomers, and conductive inorganic powders, such as tin oxide, electroconducting powder T-1 obtained from Mitsubishi Chemical, the tin/antimony oxides KW175 of Magnesium Electron Inc., the coated titanium oxide, electroconducting powder W-1 and W-10 of Mitsubishi, KW375 of Magnesium Electron Inc., the electroconducting white pigment of Tioxide, the electroconducting pigment of Sumimoto Cement Company, and the like as the surface conductive agents. The particle diameter of the above mentioned conductive powder is generally less than one micron, and preferably less than 0.1 micron. The effective amount of the conductive agent is, for example, from 0.1 to about 15 weight percent, and preferably ranges from about 0.5 to about 10 weight percent. Other process embodiments of the present invention relate to, for example, interfacial/free radical polymerization processes for obtaining magnetic colored encapsulated toner compositions. Further, in another process aspect of the present invention the encapsulated toners can be prepared without organic solvents as the diluting vehicle or as a reaction medium, thus eliminating explosion hazards associated therewith, and these processes, therefore, do not require expensive and hazardous solvent separation and recovery steps.

Encapsulated and cold pressure fixable toner compositions are known. Cold pressure fixable toners have a number of known advantages in comparison to toners that are fused by heat, primarily relating to the utilization of less energy since the toner compositions used can be fused at room temperature. Nevertheless, many of the prior art cold pressure fixable toner compositions, and in particular the magnetic colored toners, suffer from a number of deficiencies. Many of the prior art cold pressure fixable colored toners are insulative, and cannot effectively, it is believed, be utilized for the Delphax based inductive single component development. Also, in a number of instances some of the prior art cold pressure fixable colored toners are generally dull in color quality and do not offer a wide selection of color variety. Furthermore, some of the prior art toners do not contain a sufficient amount of magnetic materials to provide the required magnetic property for use in the Delphax ionography technology. Moreover, the above mentioned prior art toner compositions generally require high pressure for image fixing, and this usually leads to undesirably high image gloss and paper calendering problem. Furthermore, most of the prior art cold pressure fixable toners are prepared by conventional melt blending process, which process can produce larger toner sizes, generally of the order of over 20 microns in average particle diameter, and the large toner size usually does not effectively satisfy the requirements for high image resolution. Also, with some of the prior art cold pressure toner compositions, substantial image smearing can result because of their low fixing characteristics. Additionally, for encapsulated toner compositions, the preparative processes of the prior art in many instances employ organic solvents as the diluting vehicles and reaction media, and these could increase the toner's manufacturing cost because of the expensive solvent separation and recovery procedure, and the necessary precautions that have to be undertaken to prevent the solvent associated hazards. Moreover, the involvement of an organic solvent in the prior art processes also decreases the product yield per unit volume of reactor size. The solvents in many prior art processes may also have deleterious effects on toner particle morphology and bulk density as a result of their removal from the toner particles during the toner isolation stage, thus causing shrinkage or collapse of the toner particles, resulting in a toner of very low bulk density, which disadvantages are substantially eliminated with the process of the present invention in embodiments thereof. In addition, with many of the prior art conventional melt blended processes, narrowed size distribution toner particles cannot usually be obtained without the conventional particle size classification step as contrasted with the process of the present invention wherein narrowed size distribution toner particles can be obtained without the additional classification step in an embodiment thereof. Specifically, thus with the magnetic colored encapsulated toners of the present invention, control of the toner properties, such as color variety and shade, image fixing chracteristics, surface conductivity, toner mechanical integrity, shelf life, thermal stability, and the like can be desirably achieved. More specifically, with the magnetic colored encapsulated toners of the present invention in embodiments thereof, excellent color quality and a wide selection of color variety and shade can be obtained, the leaching or loss of core components from the encapsulated toner can be avoided or minimized, and image ghosting associated with ionographic transfix development is eliminated or minimized in many instances. Image ghosting is one of the common phenomena in the transfix ionographic printing processes. This refers to the unwarranted repetitious generation of images, and is related to the contamination of dielectric receiver by residual toner materials which cannot be readily removed in the cleaning process. The result is the retention of latent images on the dielectric receiver surface after cleaning, and the subsequent unwarranted development of these images. One of the common causes of image ghosting is related to the adherence of residual toner materials to the dielectric receiver during the image development process, and this is intimately related to the poor shell and core materials properties.

Also, encapsulated toners with core containing relatively high loadings of, for example, 30 to 70 weight percent of magnetic material are usually black or intensely dark in color even when bright colorants are present in the core. These toners usually cannot be effectively selected for the generation of brilliant colored images, especially images of high color quality. In addition, to be suitable for inductive single component development, especially for use in the Delphax type printers, it is desirable for the toner to possess a high saturation magnetic moment of from about 30 to about 60 emu per gram, as well as a volume resistivity in the range of about 10^3 to about 10^8 ohm-cm. The encapsulated colored toners of the present invention satisfy not only all the magnetic and resistivity requirements, but also offer other features such as high image fix, brilliant color, a wide spectrum of color variety and shade, excellent toner flow, nonagglomerating and nonghosting characteristics, and excellent suitability for pressure transfix under low pressure transfix conditions. Furthermore, the prior art encapsulated toners are not suitable for the provision of quality colored images.

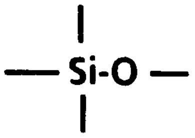
In a patentability search report, there were listed the following United States patents: 4,199,614 which relates to transparent magnetic materials and electrostatographic processes thereof, and wherein the magnetic composite particles are prepared by a solution phase thermal decomposition of certain metal carbonyls, reference the Abstract of the Disclosure, and wherein these particles may be combined with coloring dyes or pigments according to the aforementioned report; 4,238,558 and 4,245,026 relating to magnetic polymer carrier materials wherein iron carbonyl can be selected in forming the carrier particles, reference for example the Abstracts of the Disclosures; and as background interest 4,443,527; 4,448,870; 4,486,523; 4,543,312 and 4,758,490.

There is disclosed in U.S. Patent 4,803,143 a heat fusible insulative single component colored toner which is obtained by conventional melt blending milling processes. U.S. Patent 4,238,558 is directed to the production of low optical density polymer systems impregnated with very fine metal or metal oxide particles for the preparation of conventional colored toners; U.S. Patent 4,474,866 discloses an ion exchange resin with trapped fine magnetic particles which can be used for the preparation of magnetic colored toners; 4,770,968 is directed to polysiloxane butadiene terpolymer toner resins, reference for example column 4, and note the formulas of Figures 1 to 6, including Figure 28, which toners can be selected wherein silicone release oils are avoided; 4,814,253 is directed to encapsulated toners comprised of domains containing a polymer component having dispersed therein a release composition and thereover a host resin component comprised of toner resin particles and pigment particles, see for example the Abstract of the Disclosure and column 4, and note column 4 wherein there is illustrated as one of the components of the encapsulated toner domains comprised of styrene butadiene block polymers, such as Kraton, styrene copolymers, or styrene siloxanes, which components have entrapped or dissolved therein mineral oils or silicon oils; and as background interest 4,430,408 relating to developer compositions containing a fluorene modified alkyl siloxane and a surface treatment carbon black, reference the Abstract of the Disclosure, for example; 4,758,491 relating to dry toner and developer compositions with a multiphase polyorganosiloxane block or graft condensation copolymer, which provides polyorganosiloxane domains of a particular size and concentration at the toner particle surfaces; and 4,820,604 directed to toner compositions comprised of resin, pigment particles, and a sulfur containing organopolysiloxane wax, such as those of the formulas illustrated in the Abstract of the Disclosure.

There are disclosed in U.S. Patent 4,307,169 microcapsular electrostatic marking particles containing a pressure fixable core, and an encapsulating substance comprised of a pressure rupturable shell, wherein the shell is formed by an interfacial polymerization. One shell prepared in accordance with the teachings of this patent is a polyamide obtained by interfacial polymerization. Furthermore, there is disclosed in U.S. Patent 4,407,922 pressure sensitive toner compositions comprised of a blend of two immiscible polymers selected from the group consisting of certain polymers as a hard component, and polyoctyldecylvinylether-co-maleic anhydride as a soft component. Interfacial polymerization processes are also selected for the preparation of the toners of this patent. Also, there is disclosed in the prior art encapsulated toner compositions containing in some instances costly pigments and dyes, reference for example the color photocapsule toners of U.S. Patents 4,399,209; 4,482,624; 4,483,912 and 4,397,483.

Moreover, illustrated in U.S. Patent 4,758,506, the disclosure of which is totally incorporated herein by reference, are single component cold pressure fixable toner compositions, wherein the shell selected can be prepared by an interfacial polymerization process.

Disclosed in copending application U.S. Serial No. 395,689 entitled Encapsulated Toner Compositions, the disclosure of which is totally incorporated herein by reference, are encapsulated compositions containing cores comprised of a fluorocarbon-incorporated resin binder. More specifically, there is illustrated in the aforementioned application an encapsulated toner composition comprised of a core with a fluorocarbon-incorporatedresin binder, pigment or dyes, and a polymeric shell; and an encapsulated toner composition comprised of a core comprised of a fluorocarbon-incorporated resin binder derived from the copolymerization of an addition-type monomer and a functionalized fluorocarbon compound represented by Formula (I), wherein A is a structural moiety containing an addition polymerization functional group; B is a fluorine atom or a structural moiety containing an addition polymerization functional group; and x is the number of difluoromethylene functions, pigment or dyes, and a polymeric shell. Also, illustrated in U.S. Serial No. 395,677 entitled Encapsulated Toner Compositions, the disclosure of which is totally incorporated herein by reference, is an encapsulated toner composition comprised of a core comprised of pigments or dyes, and a polysiloxane-incorporated core binder resin, which core is encapsulated in a polymeric shell. Moreover, illustrated in U.S. Serial No. 419,425, the disclosure of which is totally incorporated herein by reference, encapsulated toners with a soft core comprised of silane modified polymer resin, a colorant, and a polymeric shell thereover. Specifically, in one embodiment there is disclosed in the aforementioned copending applicaton encapsulated toners comprised of a core containing a silane-modified polymer resin, preferably obtained by free radical polymerization, silane-modified pigment particles or dyes, and thereover a shell preferably obtained by interfacial polymerization. The copending application U.S. Serial No. 419,425, in one embodiment is directed to an encapsulated toner composition comprised of a core comprised of the polymer product of a monomer or monomers, and a polyfunctional organosilicon reagent, and more specifically wherein the core is comprised of a silane-modified polymer resin having incorporated therein an oxysilyl (I), a dioxysilyl (II), or a trioxysilyl (III) function of the following formula, pigment dye particles or mixtures thereof; and a polymeric shell.



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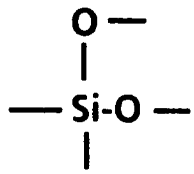
(I)



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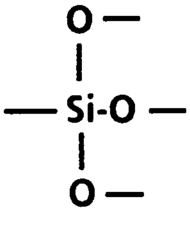
(II)



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(III)

The aforementioned toners can be prepared by a number of different processes including the interfacial/free-radical polymerization process which comprises (1) mixing or blending of a core monomer or monomers, up to 10 in some embodiments, a functionalized organosilane, a free radical initiator or initiators, pigment, and a shell monomer or monomers; (2) dispersing the resulting mixture of pigmented organic materials by high shear blending into stabilized microdroplets in an aqueous medium with the assistance of suitable dispersants or emulsifying agents; (3) thereafter subjecting the aforementioned stabilized microdroplets to a shell forming interfacial polycondensation; and (4) subsequently forming the core resin binder by heat induced free radical polymerization within the newly formed microcapsules. The shell forming interfacial polycondensation is generally accomplished at ambient temperature, but elevated temperatures may also be employed depending on the nature and functionality of the shell monomer selected. For the core polymer resin forming free-radical polymerization, it is generally effected at a temperature of from ambient temperature to about 100 °C, and preferably from ambient or room temperature, about 25 °C temperature to about 85 °C. In addition, more than one initiator may be utilized to enhance the polymerization conversion, and to generate the desired molecular weight and molecular weight distribution.

Accordingly, there is a need for encapsulated toner compositions with many of the advantages illustrated herein. More specifically, there is a need for colored encapsulated toners wherein image of brilliant color quality and excellent resolution can be obtained. Also, there is a need for pressure fixable magnetic colored encapsulated toners which provide high quality colored images with excellent image fix levels, for example over 70 percent at low fixing pressure of, for example, 2,000 psi. Moreover, there is a need for colored encapsulated toners that can be selected for inductive single component development processes such as those utilized in the commercial Delphax printers. There is also a need for a conductive magnetic colored encapsulated toner which is suitable for highlight color imaging processes. Additionally, there is a need for magnetic colored encapsulated toners, wherein the cores are comprised of certain magnetic materials that minimize, or avoid interference with the color quality of the colorants. Furthermore, there is a need for colored encapsulated toners, which possess excellent toner physical properties such as no toner agglomeration, and long shelf life exceeding, for example, 12 months. There is also a need for magnetic colored encapsulated toners which can be utilized in the Delphax based ionographic imaging members without or minimization of the problems of image ghosting and toner agglomeration in the developer housing. Also, there is a need for magnetic colored encapsulated toners that have been surface treated with conductive additives such as conductive metal oxide powders and the like to impart to their surface certain conductive characteristics, such as a toner volume resistivity of from about 10^3 ohm-cm to about 10^8 ohm-cm. Furthermore, there is also a need for simple and economic processes for the preparation of pressure fixable, conductive magnetic colored encapsulated toners. Specifically, there is a need for interfacial/free radical polymerization processes for magnetic colored encapsulated toner compositions wherein explosion prone organic solvents are eliminated in some embodiments. Moreover, there is a need for a process that provides enhanced flexibility in the design of the shell and core materials for pressure fixable magnetic colored encapsulated toners, and flexibility in controlling the toner physical properties such as surface conductivity, bulk density, particle size, and size dispersity.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide encapsulated toner compositions with many of the advantages illustrated herein.

In another object of the present invention there are provided colored, excluding black, encapsulated toner compositions comprised of a core comprised of a polymer resin, or a plurality of polymer resins preferably obtained by free radical polymerization, colored pigments and/or dyes, a colorless or lightly colored powdered iron, cobalt, nickel, magnesium, manganese, zinc, and alloys and oxides thereof, and the like, which possess a high saturation magnetic moment, and a whitener powder comprised of white inorganic material; and thereover a polymeric shell prepared, for example, by interfacial polymerization and wherein the shell may have incorporated therein a polyether or silane moiety, and wherein the toner's surface is coated with a layer of conductive agent.

Another objective of the present invention is the provision of colored encapsulated toner compositions which are suitable for the inductive single component development systems, such as the Delphax apparatuses.

An additional object of the present invention is the provision of pressure fixable colored encapsulated toners which can be selected for use in transfix ionographic imaging systems wherein image ghosting is eliminated in some embodiments, or minimized in other embodiments.

Further, another object of the present invention is the provision of colored encapsulated toners which possess excellent thermal and mechanical stability, and wherein the problem of toner agglomeration is eliminated.

Another object of the present invention is the provision of pressure fixable magnetic colored encapsulated toners that can be selected for highlight color processes and wherein images of improved color quality are obtained as compared to a number of known pressure fixable magnetic colored toners.

Also, another object of the present invention is the provision of colored encapsulated toners wherein core component leaching or loss is eliminated in some embodiments, or minimized in other embodiments.

Moreover, another object of the present invention is the provision of colored encapsulated toners wherein image offsetting is eliminated in some embodiments, or minimized in other embodiments.

Additionally, another object of the present invention is the provision of colored encapsulated toners with extended shelf life.

Further, another object of the present invention is the provision of colored encapsulated toners with excellent release properties.

Also, another object of the present invention is the provision of colored encapsulated toners with a core containing an iron powder which is available from BASF, and is commercially known as Sicopur 4068 iron powder.

It is another object of the present invention to provide colored encapsulated toners wherein contamination of the imaging member, such as a dielectric receiver or a photoreceptor, is eliminated or minimized.

Another object of the present invention is the provision of encapsulated toners that can be selected for colored imaging processes, especially highlight color processes, wherein cold pressure fixing is selected.

In another object of the present invention, there are provided simple and economical processes for magnetic colored encapsulated toner compositions prepared by an interfacial/free radical polymerization process in which the shell is generated by interfacial polymerization, and the core resin is formed by free radical polymerization.

Another object of the present invention resides in the provision of pressure fixable colored encapsulated toner compositions which provide a high image fix level of, for example, over 70 percent at a relatively low fixing pressure of, for example, 2,000 psi.

A further objective of the present invention is to provide colored encapsulated toner compositions which are suitable for duplex imaging applications.

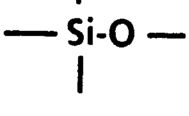
In another feature of the present invention there are provided colored encapsulated toners which contain a colorless iron oxide magnetite which has been treated with an iron carbonyl.

Additionally, in another feature of the present invention there are provided colored encapsulated toners with average particle diameters of from 10 to about 17 microns.

Also, in another feature of the present invention there are provided colored encapsulated toners with pigments, such as PV Fast Blue, Helogen Blue, Sudan Blue, Neopen Blue, Lithol Scarlet, Fanal Pink, Hostperm Pink, Novaperm Yellow, Sico Yellow, Helogen Green, and the like.

These other objects and features of the present invention can be accomplished in embodiments thereof by the provision of toners and more specifically encapsulated toners. In one embodiment of the present invention, there are provided colored encapsulated toners comprised of a core comprised of a polymer resin, pigment or dye, a colorless or lightly colored magnetic material of high magnetic saturation moment of over 70 emu per gram, and a whitener; and thereover a polymeric shell, which shell surface can be coated with a layer of conductive powder such as conductive metal oxides, and the like.

The present invention in one embodiment is directed to an encapsulated colored toner composition comprised of a core comprised of a polymer resin obtained by free radical polymerization of a monomer or monomers, colorant, excluding black colorant, or mixtures of colorants, and a colorless or lightly colored magnetic material such as the iron powder, Sicopur 4068 of BASF, and a whitening agent, and wherein the core is encapsulated in a polymeric shell preferably obtained by interfacial polymerization, and wherein the toner is rendered conductive with a layer of surface conductive additives such as a conductive powder comprised of very fine conductive metal oxides of tin, titanium, silicon, and the like. The shell of the toner composition of the present invention may have incorporated therein a polyether moiety or an oxysilyl (I), a dioxysilyl (II), or a trioxysilyl (III) function of the following formula



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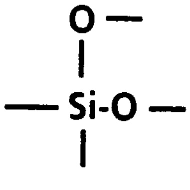
(I)



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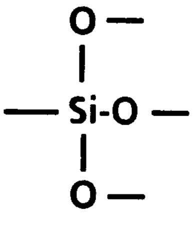
(II)



$$-\overset{\overset{\text{O}-}{|}}{\underset{\underset{\text{O}-}{|}}{\text{Si}}}\text{-O}-$$

(III)

The aforementioned toners of the present invention can be prepared by a number of different processes including the interfacial/free radical polymerization process which comprises (1) mixing or blending of a core monomer or monomers, up to 10 in some embodiments, a free radical initiator or initiators, colorant, a colorless or lightly colored magnetic material such as the iron powder, Sicopur 4068 of

BASF, a whitener such as powdered calcium carbonate, tin oxide, titanium oxide, zinc oxide, zinc stereate or the like, and an oil-soluble shell monomer or monomers; (2) dispersing the resulting mixture by high shear blending into stabilized microdroplets in an aqueous medium with the assistance of suitable dispersants or emulsifying agents; (3) thereafter subjecting the aforementioned stabilized microdroplets to a shell forming interfacial polycondensation by adding a water soluble shell monomer which reacts with the oil soluble shell monomer at the microdroplet water interface; (4) subsequently forming the core resin binder by heat induced free radical polymerization within the newly formed microcapsules; (5) subjecting the resultant encapsulated particles to washing and drying; and (6) optionally coating the encapsulated particles with surface release and conductive powder by dry blended process to provide a volume resistivity in the range of 103 to 108 ohm-cm, for example. The shell forming interfacial polycondensation is generally accomplished at ambient temperature, but elevated temperatures may also be employed depending on the nature and functionality of the shell monomer selected. For the core polymer resin forming free radical polymerization, it is generally effected at a temperature of from ambient temperature to about 100° C, and preferably from ambient or room temperature, about 25° C temperature to about 90° C. In addition, more than one initiator may be utilized to enhance the polymerization conversion, and to generate the desired molecular weight and molecular weight distribution.

Further, in accordance with the present invention there are provided processes for pressure fixable colored encapsulated toner compositions which are obtained without using organic solvents as the diluting vehicles or as reaction media. These processes involve dispersing a mixture of organic materials, colorants and magnetic material to form stabilized microdroplets in an aqueous medium containing a dispersant or emulsifying agent. The above-mentioned mixture is comprised of from about 20 to about 90 weight percent of core monomer or monomers, about 1 to 20 weight percent of a colorant or colorants, from about 30 to about 60 weight percent of a colorless or lightly colored magnetic material, and a whitener such as an inorganic oxide powder of from about 1 to about 25 weigth percent, and a shell forming monomer component of from about 2 to 25 weight percent, and a free radical initiator. The shell formation around the dispersed, stabilized microdroplets via interfacial polycondensation is initiated by adding to the reaction mixtures a water soluble shell forming monomer component. Subsequently, the reaction mixture is subjected to heating to initiate free radical polymerization to form the desired core polymer resin within the newly formed microcapsules. The encapsulated particles produced are washed with water, dried, and dry blended with surface additives comprised of conductive and release agents. In general, about 0.1 to about 15 weight percent of conductive agent in the form of very fine powder is employed, while from about 0 to about 10 weight percent of surface release agent is utilized. In one specific embodiment, the toner of the present invention can be rendered insulative without the application of the surface conductive coating, and which toner can be selected for use in xerographic development wherein image toning and transfer are accomplished electrostatically, and image fixing is achieved in a separate step with a pressure roll.

Examples of core monomers present in effective amounts, for example from about 20 to about 90 weight percent, include, but are not limited to, styrenes, methacrylates, acrylates, the copolymeric derivatives thereof, mixtures thereof and the like; and more specifically, addition monomers that can be selected as the core monomers of the present invention include, methyl acrylate, methyl methacrylate, propyl acrylate, propyl methacrylate, butyl acrylate, butyl methacrylate, hexyl acrylate, pentyl acrylate, pentyl methacrylate, hexyl acrylate, hexyl methacrylate, cyclohexyl acrylate, cyclohexyl methacrylate, lauryl acrylate, lauryl methacrylate, stearyl acrylate, stearyl methacrylate, benzyl acrylate, benzyl methacrylate, ethoxypropyl acrylate, ethoxypropyl methacrylate,heptyl acrylate, heptyl methacrylate, isobutyl acrylate, isobutyl methacrylate, methylbutyl acrylate, methylbutyl methacrylate, tolyl acrylate, tolyl methacrylate, styrene, dodecyl styrene, hexyl methyl styrene, nonyl styrene, tetradecyl styrene, other substantially equivalent addition monomers, and the like.

As colored pigments present in an effective amount such as, for example, from about 1 to about 20 weight percent, and preferably from about 3 to about 10 weight percent, there can be selected PV fast blue available from Hoescht Corporation, Helogen Blue available from BASF, Sudan Blue, Lithol Scralet available from BASF, Fanal Pink, Hostaperm Pink, Novaperm Yellow, Sico Yellow, Luna Yellow, Helogen Green, Levanox Green, Bayplast Green, Sicopal Brown, Heliogen Blue L6900, D6840, D7080, D7020, Pylam Oil Blue and Pylam Oil Yellow, Pigment Blue 1 available from Paul Uhlich & Company Inc., Pigment Violet 1, Pigment Red 48, Lemon Chrome Yellow DCC 1026, E.D. Toluidine Red and Bon Red C available from Dominion Color Corporation Ltd., Toronto, Ontario, NOVAperm Yellow FGL, Hostaperm Pink E from Hoechst, Cinquasia Magenta available from E.I. DuPont de Nemours & Company, and the like. Illiustrative examples of primary colorants (cyan, magenta, yellow) that can be selected include the magenta colorants such as, for example, 2,9-dimethyl-substituted quinacridone and anthraquinone dye identified in the Color Index as CI 60710, CI Dispersed Red 15, diazo dye identified in the Color Index as CI 26050, CI Solvent

Red 19, and the like; the cyan colorants such as copper tetra-(octadecyl sulfonamido) phthalocyanine, x-copper phthalocyanine pigment listed in the Color Index as CI 74160, CI Pigment Blue, and Anthrathrene Blue identified in the Color Index as CI 69810, Special Blue X-2137, and the like; and the yellow colorants such as diarylide yellow 3,3-dichlorobenzidene acetoacetanilides, a monoazo pigment identified in the Color Index as CI 12700, CI Solvent Yellow 16, a nitrophenyl amine sulfonamide identified in the Color Index as Foron Yellow SE/GLN, CI Dispersed Yellow 33 2,5-dimethoxy-4-sulfonanilide phenylazo-4'-chloro-2,5-dimethoxy acetoacetanilide, and Permanent Yellow FGL.

As the magnetic material, there is selected in an effective amount, such as, for example, from about 20 to about 60, and preferably from about 30 to about 50 weight percent, a colorless or lightly colored magnetic material which does not significantly interfere with the coloration of the colorants. Illistrative examples of colorless or lightly colored magnetic materials that can be selected include iron powder, Sicopur 4068 of BASF; Magnox's brown magnetite, TMB-50; brown iron oxide, LODOMS; ferrites of magnesium; nickel, magnesium, manganese, zinc and alloys and oxides thereof, and the like. One preferred magnetic material for the encapsulated toner composition of the present invention is Sicopur 4068 iron powder, which has the following characteristics as reported by BASF, (1) high magnetic saturation moment of about 98 emu per gram; (2) particle size of about 2 to about 6 micron in average particle diameter; (3) grayish in color; and (4) particle shape ranging from being spherical to elliptical to acicular. Typical whitening agents are white inorganic oxides such as oxides of tin and titanium, and the like with the amount of the whitening agent being, for example, in the range of, for example, from about 1 to about 30 weight percent, and preferably from 5 to 20 weight percent.

Examples of shell polymers present in various effective amounts such as, for example, from about 5 to about 25 weight percent include polyureas, polyamides, polyesters, polyurethanes, mixtures thereof, and other similar polycondensation products including the reaction products of polyether polyisocyanate prepolymers with polyamines, reference copending application U.S. Serial No. 402,306; the reaction products of polysiocyanates with functionalized organosilanes and polyamines, reference copending application U.S. Serial No. (D/90066 - not yet assigned) with polyamines, the disclosures of these applications being totally incorporated herein by reference. The shell amounts are generally from about 5 to about 25 weight percent of toner, and have a thickness generally, for example, of less than about 5 microns, and more specifically from about 0.1 micron to about 3 microns in an embodiment of the present invention. Other shell polymers, shell amounts, and thicknesses may be selected. The polymeric shells are usually prepared by interfacial polymerization processes such as those illustrated in U.S. Patents 4,000,087; 4,307,169 and 3,429,827, the disclosures of each of these patents being totally incoporated herein by reference.

The oil soluble shell forming monomer components present in the microdroplet phase are in embodiments comprised of diisocyanates, diacyl chloride, bischloroformate, together with appropriate polyfunctional crosslinking agents such as triisocyanate, triacyl chloride, and the like. Illustrative examples of the oil soluble shell monomer components include benzene diisocyanate, toluene diisocyanate, diphenylmethane diisocyanate, cyclohexane diisocyanate, hexane diisocyanate, Uniroyal Chemical's diphenylmethane diisocyanate-based liquid polyether Vibrathanes such as B-635, B-843, and toluene diisocyanate-based liquid polyether Vibrathanes such as B-604, B-614, Mobay Chemical Corporation's liquid polyether isocyanate prepolymers, DESMODUR E-21, E-21A, 744, AMODUR CB-60, MONDUR CB-75, MONDUR MR, MONDUR MRS 10, adipoyl chloride, fumaryl chloride, suberoyl chloride, succinyl chloride, phthaloyl chloride, isophthaloyl chloride, terephthaloyl chloride, ethylene glycol bischloroformate, diethylene glycol bischloroformate, mixtures thereof, and the like. The water soluble, shell forming monomer components which are added to the aqueous phase can be a polyamine or polyol including bisphenols, the nature of which is dependent on the shell characteristics desired, for example. Illustrative examples of water soluble shell monomers that react with the aforementioned diisocyanates, and the like include ethylenediamine, triethylenediamine, diaminotoluene, diaminopyridine, bis(aminopropyl)piperazine, mixtures of polyamines and aminoalklyltrialkoxy silane, aminoalkylalkyldialkoxy silane, aminoalkyldialkylalkoxy silane, p-aminoaryltrialkoxy silane, N-(aminoalkyl)aminoalkylalkyldialkoxy silane, N-(aminoalkyl)aminoalkyltrialkoxy silane, 3-[bis(hydroxyalkyl)amino]alkyltrialkoxy silane, trialkoxysilylalkyldialkylenetriamine, 1,3-bis(hydroxyalkyl)-tetraalkyldisiloxane, or the like, bisphenol A, bisphenol Z, and the like. When desired, a water soluble crosslinking component such as triamine or triol can also be added to improve the mechanical strength of the shell structure.

In one embodiment of the present invention, there is provided a process for the preparation of improved encapsulated toner compositions, which process comprises mixing and dispersing a core monomer or monomers, a free radical initiator or initiators, colored, excluding black, pigment particles or dyes, a colorless or lightly colored magnetic material as illustrated herein, a whitener, an oil soluble shell monomer component, into microdroplets of specific droplet size and size distribution in an aqueous medium containing a dispersant or stabilizer wherein the volume average diameter of the microdroplet can be adjusted to be preferably from about 5 microns to about 30 microns, and its volume average droplet size dispersity can be controlled to be preferably less than about 1.4, as determined from Coulter Counter measurements of the microcapsule particles after encapsulation; forming a microcapsule shell around the microdroplets via interfacial polymerization by adding a water soluble shell forming monomer component; affecting a free radical polymerization to form a core resin binder within the newly formed microcapsules by, for example, heating the reaction mixture from room temperature to about 100° C for a period of from about 1 to about 10 hours; and subsequently washing and drying the resultant encapsulated particles. Stabilizers selected for the process of the present invention include water soluble polymers such as poly(vinyl alcohols), methyl cellulose, hydroxypropyl cellulose and the like. Illustrative examples of free radical initiators selected for the preparation of the toners of the present invention include azo compounds such as 2-2'-azodimethylvaleronitrile, 2-2'-azoisobutyronitrile, azobiscyclohexane-nitrile, 2-methylbutyronitrile or mixtures thereof with the quantity of initiator(s) being, for example, from about 0.01 percent to about 10 percent by weight of that of core monomer(s). Interfacial polymerization processes selected for toner shell formation and shells thereof are as illustrated, for example, in U.S. Patents 4,000,087 and 4,307,169, the disclosures of which are totally incorporated herein by reference.

The toner compositions can be rendered conductive by conventional dry blending process with a suitable conductive powder in an effective amount of from about 0.1 to about 15 weight percent. In general, a volume resistivity of about 10^3 to 10^8 ohm-cm, preferably from about 104 to 10^7 ohm-cm, is desired for the Delphax based ionographic transfix development. Illustrative examples of conductive reagents include metal halides such as copper iodide, and potasium iodide, conductive powdered oxides and mixed oxides of aluminum, barium, chromium, germanium, indium, magnesium, molybdenum, nickel, silicon, titanium, tin, zirconium, and a combination of two or more of these metals, and the like, and wherein the SPECIFIC resistivity of the powder is less than 100 ohm-cm, and preferably less than 50 ohm-cm. Specific examples of commercial conductive powders that can be selected for the compositions of the present invention include conductive powders available from Magnesium Electron Inc., Mitsubishi, Sumimoto Cement Company, and Tioxide as electroconducting powder T-1 (Mitsubishi), the tin/antimony oxides KW175 (Magnesium Electron Inc.), the coated titanium oxide, electroconducting powder W-1 and W-10 (Mitsubishi), KW375 (Magnesium Electron Inc.), electroconducting white pigments (Tioxide), electroconducting pigments (Sumimoto Cement Company). Surface release and/or flow agents may also be used to provide the release and flow properties to the toner. Illustrative examples of these agents that can be selected for the toner compositions of the present invention include, for example, metal salts, metal salts of fatty acids, colloidal silicas, mixtures thereof, and the like, which additives are usually present on the surface of the toner in an amount of from about 0.1 to about 5 weight percent, reference U.S. Patents 3,590,000; 3,720,617; 3,655,374 and 3,983,045, the disclosures of which are totally incorporated herein by reference. Preferred additives include zinc stearate, magnesium stearate, and Aerosil R972.

The following examples are being submitted to further define various aspects of the present invention. These examples are intended to be illustrative only and are not intended to limit the scope of the present invention.

EXAMPLE I

The following example illustrates the preparation of a 17.1 micron red encapsulated toner using Sicopur 4068 iron powder and a conductive tin oxide agent. This pressure fixable encapsulated toner is suitable for inductive single component development.

A mixture of n-lauryl methacrylate (113.0 grams), Isonate 143 L (42.0 grams), Desmodur E-21 (5.7 grams), Vazo 52 (1.6 grams), Vazo 64 (1.6 grams) was homogenized at 4,000 rpm using an IKA T-50 polytron with a G45/M probe for 30 seconds. To this mixture were added titanium dioxide powder (rutile form, 90 grams), Sicopur 4068 iron powder (245.0 grams) and Lithol Scarlet pigment (29.0 grams), followed by homogenization at 8,000 rpm for 3 to 5 minutes. To the resulting slurry was then added one liter of a 0.10 percent aqueous poly(vinylalcohol) solution, and the mixture was then homogenized at 9,000 rpm for 2 minutes. The resulting dispersion was transferred into a two liter kettle equipped with a mechanical stirrer. Bis(3-aminopropyl)piperazine (33.0 grams) was added, and the mixture was stirred for one hour at room temperature. Subsequently, the reaction mixture was heated in an oil bath with the temperature of the bath being raised from ambient temperature to 90° C over a period of 45 minutes, and then held at this temperature for another 6 hours. After cooling to room temperature, the mixture was allowed to remain at room temperature to permit the encapsulated particles to settle to the bottom of the reaction kettle. The separated particles were washed repeatedly with water until the aqueous phase was clear. The wet encapsulated particles were sieved through a 180 micron screen, and freeze dried to provide 350.0 grams of red encapsulated particles.

A mixture of 120.0 grams of the above prepared red encapsulated particles and 3.0 grams of conductive tin oxide doped with antimony oxide powder (volume resistivity of 1 to 5 ohm-cm, available from Mitsubishi as ECP T-1) was dry blended in a dry blender at 3,000 rpm for 4 minutes. The blending was continued for another 15 minutes with an additional 6.0 grams of the above ECP T-1 conductive powder, and then with 1.2 grams of zinc stearate for 1 minute, followed by sieving through a 63 micron screen. The resulting red encapsulated toner product has a volume average particle diameter of 17.1 microns and a particle size distribution of 1.34 as obtained using the Coulter Counter Model ZM, available from Coulter Electronics, Inc.

The toner's volume resistivity was measured on powdered samples, which were packed in a 1 cm^3 cell using a horseshoe magnet placed beneath the cell. Two opposite walls of the cell are 1 centimeter x 1 centimeter conductive metal plates. The other walls and the bottom of the cell are 1 centimeter x 1 centimeter, and are comprised of an insulating material. A voltage of 10 volts is applied across the plates, and the current flow through the plates is measured using an electrometer. The device is standardized using a nickel standard whose saturation magnetic moment is known (55 emu/gram). The nickel sample is magnetized between two magnetic pole faces with a saturating magnetic field of 2,000 Gauss, such that the induced magnetic field is perpendicular to one of the 1 centimeter faces of the cell. The integrated current that is induced when the nickel sample is removed from the saturating magnetic field is measured. Next, the integrated current induced by a toner sample under identical conditions is also measured. The toner's saturation magnetic moment is then obtained by referencing its induced current per gram of sample to that of the nickel sample. For the toner of this example, the saturation magnetic moment was measured to be 49 emu per gram, and its volume resistivity was measured to be 7.1×10^7 ohm-cm.

The above prepared toner was evaluated in a Xerox Corporation 4060™ printer. The images developed were transfixed onto paper with a transfix pressure of 2,000 psi. Print quality was evaluated from a checkerboard print pattern. The image optical density was measured with a standard integrating densitometer. Image fix was measured by the standardized tape pull method, and is expressed as a percentage of the retained image optical density after the tape test relative to the original image optical density. Image smearing was evaluated qualitatively by hand rubbing the fused checkerboard print using a blank paper under an applied force for a specific cycle time, and viewing the surface cleanliness of nonprinted and printed areas of the page. Image ghosting was evaluated visually. For the above prepared toner, the image fix level was 85 percent, and no image smear and no image ghosting were observed in this machine testing. The toner displayed a resistance to agglomeration even when heated at 55° C for 48 hours.

EXAMPLE II

The following example describes the preparation of a 18.8 micron pressure fixable blue encapsulated toner using Sicopur 4068 iron powder and conductive tin oxide agent.

A blue encapsulated toner was prepared in accordance with the procedure of Example I except that Hostaperm blue pigment (Hoechst) was employed in place of Lithol Scarlet pigment. The wet encapsulated particles were sieved through a 180 micron screen, and freeze dried to provide 320.0 grams of blue encapsulated particles. The dry encapsulated particles were dry blended according to the procedure of Example I, yielding a blue encapsulated toner with a volume average particle diameter of 18.8 microns and a particle size distribution of 1.36. The toner's saturation magnetic moment was measured to be 50 emu per gram, and the toner volume resistivity was found to be 9.5×10^7 ohm-cm.

The above prepared toner was evaluated according to the procedure of Example I. For this toner, the image fix level was 81 percent, and no image ghosting and no image smear were observed in this machine testing. The toner displayed a resistance to agglomeration when heated at 55° C for 48 hours.

EXAMPLE III

A blue encapsulated toner with a polysiloxane containing poly(lauryl methacrylate) core resin and Sicopur 4068 iron powder was prepared as follows:

The toner was prepared in accordance with the procedure of Example I with the exception that a mixture of 103.0 grams of lauryl methacrylate and 10.0 grams of methacryloxypropyl terminated polydimethyl siloxane (viscosity, 1,500 to 2,500 centistokes) was employed in place of 113.0 grams of lauryl methacrylate. In addition, 25.0 grams of Heliogen blue pigment (BASF) was utilized instead of 29.0 grams of

Lithol Scarlet pigment. The encapsulated particles were dry blended with zinc stearate and conductive powdered tin oxide doped with antimony oxide, affording a blue encapsulated toner with a volume average particle diameter of 13.2 microns and a particle size distribution of 1.37. The toner's saturation magnetic moment was measured to be about 42 emu per gram, and the toner volume resistivity was found to be 6.3 X 10^7 ohm-cm. For this toner, the image fix level was 83 percent, and no image smear and no image ghosting were observed after 2,000 prints. This toner did not evidence agglomeration on storage for about six months..

EXAMPLE IV

A green encapsulated toner with a poly(lauryl methacrylate) core resin and Sicopur 4068 iron powder material was prepared in accordance with the procedure of Example I except that Hostaperm Green pigment (Hoechst) was utilized in place of Lithol Scarlet pigment. The green encapsulated toner as obtained in this manner has a volume average diameter of 14.1 microns and a particle size distribution of 1.37. The toner's volume resistivity was 1.1 X 10^7 ohm-cm, and its saturation magnetic moment was measured to be 48 emu per gram. The toner was evaluated in accordance with the procedure of Example I, and substantially similar results were obtained.

EXAMPLE V

A magenta encapsulated toner with a (lauryl methacrylate-stearyl methacrylate) copolymeric core resin and Sicopur 4068 iron powder material was prepared in accordance with the procedure of Example I except that a mixture of 56.5 grams each of lauryl methacrylate and stearyl methacrylate was utilized instead of 113.0 grams of lauryl methacrylate. In addition, Lithol Scarlet pigment was replaced with Hostaperm Pink pigment (Hoechst). The magenta toner as obtained in this manner has a volume average particle diameter of 18.3 microns and a particle size distribution of 1.33. This toner has a saturation magnetic moment of 49 emu per gram, and a volume resistivity of 2.4 X 10^7 ohm-cm.

This toner provided a tape fix level of 91 percent, and no image smear and no image ghosting were observed during machine evaluation. No signs of toner agglomeration were observed with this toner after six months of storage.

EXAMPLE VI

A brown colored encapsulated toner was prepared in accordance with the procedure of Example III using 300 grams of Magnox iron oxide, TMB-50 and 5.0 grams of Microlith brown pigment instead of Sicopur 4068 iron powder and Heliogen Blue pigment (BASF), respectively. The resulting encapsulated toner has a volume average particle diameter of 15.3 micron and a particle size distribution of 1.37. The toner has a volume resistivity of 3.6 X 10^7 ohm-cm and a saturation magnetic moment of 45 emu per gram. For this toner, the image fix was 79 percent with no signs of image smear, image ghosting and toner agglomeration.

EXAMPLE VII

The following procedure illustrates the preparation of a 13.8 blue encapsulated toner with a polysiloxane containing core resin and a silane modified shell.

A mixture of lauryl methacrylate (103.0 grams), methacryloxypropyl terminated polydimethyl siloxane (10.1 grams; viscosity, 1,500 to 2,500 centistokes) Isonate 143L (42.0 grams), Desmodur E-21 (5.7 grams), Vazo 52 (1.6 grams), and Vazo 64 (1.6 grams) was homogenized at 4,000 rpm using an IKA T-50 polytron with a G45/M probe for 30 seconds. To this mixture were added titanium dioxide powder (rutile form, 90 grams), Sicopur 4068 iron powder (245.0 grams) and Heliogen Blue pigment (25.0 grams; BASF), followed by homogenization at 8,000 rpm for 3 to 5 minutes. To the resulting slurry was then added one liter of a 0.10 percent aqueous poly(vinylalcohol) solution, and the mixture was then homogenized at 9,000 rpm for 2 minutes. The dispersion was transferred into a two liter reaction kettle, and into this mixture was added bis-(3-aminopropyl)piperazine (30.0 grams). The resulting mixture was stirred at room temperature for 15 minutes, followed by addition of 3-aminopropyltrimethoxysilane (5.5 milliliters). After the addition, the mixture was allowed to react at room temperature for 1 hour. Subsequently, the procedure of Example I for the free radical polymerization and the work up was repeated to yield a blue toner. The prepared blue toner had a volume average particle diameter of 13.8 microns and a particle size distribution of 1 .34. This toner has a saturation magnetic moment of 43 emu per gram, and a volume resistivity of 7.2 X 10^7 ohm-cm. The toner was machine tested in the Delphax S6000™ printer, and substantially similar results were obtained as reported in Example I.

EXAMPLE VIII

A red encapsulated toner was prepared in accordance with the procedure of Example III using 29.0 grams of Lithol Scarlet pigment instead of Heliogen Blue pigment (BASF). The red encapsulated toner product has a volume average particle diameter of 14.7 microns and a particle size distribution of 1.34. Its volume resistivity was found to be 7.8 X 10^7 ohm-cm and its saturation magnetic moment, 44 emu per gram. The toner was evaluated in a Delphax S6000™, and substantially similar results were obtained.

EXAMPLE IX

An orange encapsulated toner was prepared in accordance with the procedure of Example I using a mixture of 150.0 grams of Sicopur 4068 iron powder, 150.0 grams of titanium dixoide and 29.0 grams of Bayplast Orange pigment (Bayer) in place of a mixture of 245.0 grams of Sicopur 4068 iron powder, 90.0 grams of titanium dioxide powder and 29.0 grams of Lithol Scarlet pigment. In addition, 0.08 percent of aqueous poly(vinyl alcohol) solution was utilized instead of 0.10 percent of aqueous poly(vinyl alcohol) solution. The orange toner product had a volume average particle diameter of 19.8 micron and a particle size distribution of 1.32. This toner had a volume resistivity of 2.3 X 10^7 ohm-cm and a saturation magnetic moment of 33 emu per gram. The toner was evaluated in a Delphax S6000™, and substantially similar results were obtained.

EXAMPLE X

A yellow encapsulated toner was prepared in accordance with the procedure of Example IX using Novaperm Yellow pigment (Hoechst) instead of Bayplast Orange pigment. The yellow toner obtained had a volume average particle diameter of 18.7 microns and a particle size distribution of 1.34. The toner had a volume resistivity of 5.1 X 10^7 ohm-cm and a saturation magnetic moment of 32 emu per gram. This toner was evaluated in a Delphax S6000™, and substantially similar results were obtained.

Other modifications of the present invention may occur to those skilled in the art subsequent to a review of the present application, and these modifications are intended to be included within the scope of the present invention.

Claims

1. An encapsulated toner composition comprised of a core comprised of a polymer resin, color pigment, dye or mixtures thereof, a colorless magnetic material, and a whitening agent; which core is encapsulated in a polymeric shell.

2. An encapsulated toner composition comprised of a core comprised of a polymer resin, color pigment, dye or mixtures thereof, a light colored magnetic material, and a whitening agent; which core is encapsulated in a polymeric shell.

3. An encapsulated toner composition comprised of a core comprised of a polymer resin, color pigment, dye or mixtures thereof, a colorless or lightly colored magnetic material, and a whitening agent; which core is encapsulated in a polymeric shell and wherein the shell has optionally incorporated therein or thereon surface additives.

4. An encapsulated toner in accordance with claim 3 wherein the surface additive is selected from the group consisting of conductive components and release components.

5. An encapsulated toner composition comprised of a core comprised of a polymer resin, color pigment, a substantially colorless magnetic material, and a whitening agent, which core is encapsulated in a polymeric shell.

6. An encapsulated toner composition comprised of a core comprised of a polymer resin, color pigment, a

substantially colorless magnetic material, and an inorganic powder whitening agent, which core is encapsulated in a polymeric shell.

7. A colored magnetic encapsulated toner composition comprised of a core comprised of a polymer resin, color pigment, dye or mixtures thereof, a lightly colored magnetic material, and a whitening agent of inorganic powder, which core is encapsulated in a polymeric shell, and wherein the shell has optionally incorporated on the shell surface or within the shell polymer a conductive powder, and a release agent.

8. An inductive single component colored encapsulated toner composition comprised of a core comprised of a polymer resin or a plurality of polymer resins, color pigment, dye or mixtures thereof, a colorless or lightly colored magnetic material of high magnetic saturation moment and a whitening agent, which core is encapsulated in a polymeric shell obtained by interfacial polymerization, and wherein the toner is optionally rendered conductive by application to the toner's surface of a layer of conductive powder.

9. A colored magnetic encapsulated toner composition comprised of a core comprised of a polymer resin, colored pigment, excluding black, lightly colored magnetic material and an inorganic whitener, which core is encapsulated in a polymeric shell which contains polyether or siloxane moieties as integral parts of its polymer structure, and wherein the toner is optionally coated with a layer of conductive and release agents.

10. An encapsulated toner composition in accordance with claim 1 wherein the core polymer is selected from the group consisting of acrylate polymers, methacrylate polymers, styrene polymers, and their copolymers thereof.

11. An encapsulated toner composition in accordance with claim 2 wherein the core polymer is selected from the group consisting of acrylate polymers, methacrylate polymers, styrene polymers, and their copolymers.

12. An encapsulated toner composition in accordance with claim 3 wherein the core polymer is selected from the group consisting of acrylate polymers, methacrylate polymers, styrene polymers, and their copolymers.

13. An encapsulated toner composition in accordance with claim 3 wherein the core polymer is selected from the group consisting of poly(alkyl acrylate), poly(alkyl methacrylate), poly(alkyl styrene), and their copolymers thereof, and wherein alkyl contains from about 1 to about 20 carbon atoms.

14. An encapsulated toner composition in accordance with claim 8 wherein the monomer or monomers for the core polymer is selected from the group consisting of methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, propyl acrylate, propyl methacrylate, butyl acrylate, butyl methacrylate, pentyl acrylate, pentyl methacrylate, hexyl acrylate, hexyl methacrylate, heptyl acrylate, heptyl methacrylate, cyclohexyl acrylate, cyclohexyl methacrylate, lauryl acrylate, lauryl methacrylate, stearyl acrylate, stearyl methacrylate, benzyl acrylate, benzyl methacrylate, ethoxypropyl acrylate, ethoxypropyl methacrylate, methylbutyl acrylate, methylbutyl methacrylate, tolyl acrylate, tolyl methacrylate, styrene, dodecyl styrene, hexyl methyl styrene, nonyl styrene, and tetradecyl styrene.

15. An encapsulated toner composition in accordance with claim 3 wherein the magnetic material is Sicopur 4068 iron powder.

16. An encapsulated toner composition in accordance with claim 3 wherein the surface conductive agent is selected from the group consisting of conductive powdered oxides and mixed oxides of aluminum, barium, chromium, germanium, indium, magnesium, molybdenum, nickel, silicon, titanium, tin, zirconium and mixtures thereof.

17. A toner in accordance with claim 16 wherein the SPECIFIC resistivity of the toner powder is less than 100 ohm-cm.

18. A toner in accordance with claim 16 wherein the SPECIFIC resistivity of the toner powder is less than 50 ohm-cm.

19. An encapsulated toner composition in accordance with claim 16 wherein the conductive oxide is tin/antimony oxides, coated titanium oxide, or electroconducting pigments.

20. An encapsulated toner composition in accordance with claim 16 wherein the metal oxide is doped with a donor atom with the amount of dopant being present in the range of 0.1 to about 10 molar percent.

21. An encapsulated toner composition in accordance with claim 20 wherein the metal oxides are zinc oxide, tin oxide and titanium oxides doped with aluminum, antimony, bismuth, halogen, indium, niobium or tantalum.

22. An encapsulated toner composition in accordance with claim 3 wherein the magnetic material has a magnetic saturation moment of over 70 emu per gram.

23. An encapsulated toner composition in accordance with claim 3 wherein the magnetic material has a mean particle diameter of 0.1 micron to about 8 microns.

24. An encapsulated toner composition in accordance with claim 1 wherein the whitening agent is powdered aluminum oxide, barium oxide, calcium carbonate, calcium oxide, magnesium oxide, magnesium stearate, titanium oxide, tin oxide, zinc oxide, or zinc stearate.

25. An encapsulated toner composition in accordance with claim 2 wherein the whitening agent is powdered aluminum oxide, barium oxide, calcium carbonate, calcium oxide, magnesium oxide, magnesium stearate, titanium oxide, tin oxide, zinc oxide, or zinc stearate.

26. An encapsulated toner composition in accordance with claim 3 wherein the whitening agent is powdered aluminum oxide, barium oxide, calcium carbonate, calcium oxide, magnesium oxide, magnesium stearate, titanium oxide, tin oxide, zinc oxide, or zinc stearate.

27. An encapsulated toner composition in accordance with claim 4 wherein the whitenening agent is selected from the group consisting of powdered aluminum oxide, tin oxide and titanium oxide.

28. An encapsulated toner in accordance with claim 1 wherein the pigment is cyan, magneta, yellow, or mixtures thereof; blue, green, red, brown, or mixtures thereof.

29. An encapsulated toner in accordance with claim 2 wherein the pigment is a cyan pigment or dye, a magneta pigment or dye, a yellow pigment or dye, or mixtures thereof; blue, green, red, brown pigment or dye, or mixtures thereof.

30. An encapsulated toner in accordance with claim 3 wherein the pigment is a cyan pigment or dye, a magneta pigment or dye, a yellow pigment or dye, or mixtures thereof; blue, green, red, brown pigment or dye, or mixtures thereof.

31. An encapsulated toner in accordance with claim 1 wherein the pigment is PV Fast Blue, Heliogen Blue, Sudan Blue, Neopen Blue, Lithol Scarlet, Fanal Pink, Hostperm Pink, Novaperm Yellow, Sico Yellow, Luna Yellow, Heliogen Green, Levanox Green, Bayplast Green, or Sicopal Brown.

32. An encapsulated toner in accordance with claim 2 wherein the pigment is PV Fast Blue, Heliogen Blue, Sudan Blue, Neopen Blue, Lithol Scarlet, Fanal Pink, Hostperm Pink, Novaperm Yellow, Sico Yellow, Luna Yellow, Heliogen Green, Levanox Green, Bayplast Green, or Sicopal Brown.

33. An encapsulated toner in accordance with claim 3 wherein the pigment is PV Fast Blue, Heliogen Blue, Sudan Blue, Neopen Blue, Lithol Scarlet, Fanal Pink, Hostperm Pink, Novaperm Yellow, Sico Yellow, Luna Yellow, Heliogen Green, Levanox Green, Bayplast Green, or Sicopal Brown.

34. An encapsulated toner in accordance with claim 3 wherein the pigment is Heliogen Blue L6900, D6840, D7080, D7020, Pylam Oil Blue, Pylam Oil Yellow, Pigment Blue 1, Pigment Violet 1, Pigment Red 48, Lemon Chrome Yellow DCC 1026, E.D. Toluidine Red, Bon Red C, NOVA perm Yellow FGL, Hostaperm Pink E, 2,9-dimethyl-substituted quinacridone and anthraquinone dye identified in the Color

Index as CI 60710, CI Dispersed Red 15, diazo dye identified in the Color Index as CI 26050, CI Solvent Red 19, copper tetra-(octadecyl sulfonamido) phthalocyanine, x-copper phthalocyanine pigment listed in the Color Index as CI 74160, CI Pigment Blue, and Anthrathrene Blue identified in the Color Index as CI 69810, Special Blue X-2137, diarylide yellow 3,3-dichlorobenzidene acetoacetanilides, a monoazo pigment identified in the Color Index as CI 12700, CI Solvent Yellow 16, a nitrophenyl amine sulfonamide identified in the Color Index as Foron Yellow SE/GLN, CI Dispersed Yellow 33 2,5-dimethoxy-4-sulfonanilide phenylazo-4'-chloro-2,5-dimethoxy acetoacetanilide, and Permanent Yellow FGL.

35. An encapsulated toner in accordance with claim 4 wherein the conductive component is present in an amount from 0.1 to about 15 weight percent, the surface release agent is present in an amount from 0.1 to about 10 weight percent, the shell polymer is present in an amount from about 5 to about 20 weight percent, the core polymer is present in an amount from about 20 to about 90 weight percent, the colorless or lightly colored magnetic material is present in an amount from about 20 to about 60 weight percent, the whitening agent is present in an amount from about 1 to about 25 weight percent, and the pigment is present in an amount from about 1 to about 20 weight percent of the toner.

36. An encapsulated toner in accordance with claim 7 wherein the amount of conductive component is present in an amount about 0.1 to 10 weight percent, the amount of release agent is about 0.1 to about 5 weight percent, the amount of shell polymer is about 10 to about 18 weight percent, the amount of core polymer is about 20 to about 40 weight percent, the amount of colorless or lightly colored magnetic material is about 30 to about 55 weight percent, the amount of whitening agent is about 5 to about 20 weight percent, and the amount of pigment is about 1 to about 10 weight percent.

37. An encapsulated toner composition in accordance with claim 3 wherein the shell polymer contains a sane moiety derived from the reaction of the shell monomers with the sane reagent selected from the group consisting of aminoalklyltrialkoxys ilane, aminoalkylalkyldialkoxy silane, aminoalkyldialkylalkoxy silane, p-aminoaryltrialkoxy silane, N-(aminoalkyl)aminoalkylalkyldialkoxy silane, N-(aminoalkyl)-aminoalkyltrialkoxy silane, 3-[bis(hydroxyalkyl)amino]alkyltrialkoxy silane, trialkoxysilylalkyldialkylenetriamine, 1,3-bis(hydroxyalkyl)tetraalkyldisiloxane, wherein the alkyl group contains from about 1 to about 20 carbon atoms, and alkoxy group contains from about 1 to about 10 carbon atoms.

38. An encapsulated toner composition in accordance with claim 3 wherein the shell polymer contains a polyether segment derived from the polyether isocyanate shell precursor selected from the group consisting of diphenylmethane diisocyanate-based liquid polyether Vibrathanes, toluene diisocyanate based liquid polyether Vibrathanes and liquid polyether isocyanate prepolymers.

39. An encapsulated toner in accordance with claim 7 wherein the pigment is selected from the group consisting of Heliogen Blue, Pylam Oil Blue, Pylam Oil Yellow, Pigment Blue, Pigment Violet, Pigment Red, Lemon Chrome Yellow, Bon Red, NOVAperm Yellow FGL, Hostaperm Pink, Magenta 2,9-dimethyl-substituted quinacridone, Dispersed Red, Solvent Red, copper tetra-(octadecyl sulfonamido) phthalocyanine, copper phthalocyanine pigment, diarylide yellow 3,3-dichlorobenzidene acetoacetanilides, a nitrophenyl amine sulfonamide, Dispersed Yellow 2,5-dimethoxy-4-sulfonanilide phenylazo-4'-chloro-2,5-dimethoxy acetoacetanilide, and Permanent Yellow FGL.

40. An encapsulated toner in accordance with claim 1 containing surface additives.

41. An encapsulated toner in accordance with claim 40 wherein the surface additives are metal salts, metal salts of fatty acids, colloidal silicas, conductive metal oxides, or a mixture thereof.

42. An encapsulated toner in accordance with claim 41 wherein zinc stearate is selected.

43. An encapsulated toner in accordance with claim 41 wherein the conductive metal oxides are selected from the group consisting of aluminum, bismuth, chromium, germanium, magnesium, molybdenum, nickel, silicon, titanium, tin and zirconium.

44. An encapsulated toner in accordance with claim 40 wherein the additives are present in an amount of from about 1 to about 25 weight percent.

45. An encapsulated toner in accordance with claim 1 wherein the core polymer resin is prepared by free radical polymerization.

46. An encapsulated toner in accordance with claim 1 wherein the shell is prepared by interfacial polymerization.

47. An encapsulated toner in accordance with claim 1 wherein the polymeric shell is a polyurea, a polyurethane, polyamide, a polyester, or mixtures thereof, and wherein the shell polymer has optionally incorporated therein a silane or polyether moiety.

48. An encapsulated toner in accordance with claim 3 wherein the shell is comprised of the reaction product of an isocyanate and an amine.

49. An encapsulated toner in accordance with claim 3 wherein the volume resistivity of the toner composition is from about 10^3 to about 10^8ohm-cm.

50. An imaging method which comprises the formation of an image on an imaging substrate, subsequently developing the image with the toner composition of claim 1, and transferring the image to a substrate.

51. An imaging method which comprises the formation of an image on an imaging substrate, subsequently developing the image with the toner composition of claim 2, and transferring the image to a substrate.

52. An imaging method which comprises the formation of an image on an imaging substrate, subsequently developing the image with the toner composition of claim 3, and transferring the image to a substrate.

53. An imaging method which comprises the formation of an image on a dielectric substrate, subsequently developing the image with the toner composition of claim 1, and transferring the image to a substrate.

54. An imaging method which comprises the formation of an image on a dielectric substrate, subsequently developing the image with the toner composition of claim 2, and transferring the image to a substrate.

55. An imaging method which comprises the formation of an image on a dielectric substrate, subsequently developing the image with the toner composition of claim 3, and transferring the image to a substrate.

56. A process for the preparation ofthe encapsulated toners of claim 1 which comprises mixing a core monomer, or plurality of monomers, a free radical initiator, a colorant, a whitener, a substantially colorless magnetic material and an oil soluble shell monomer, or plurality of monomers; dispersing the resulting mixture by heat shear blending into stabilized microdroplets in an aqueous medium; subjecting the aforementioned stabilized droplets to a shell forming interfacial polycondensation; subsequently forming the core resin binder by heat induced free radical polymerization; and optionally subjecting the resulting encapsulated toner particles to washing and drying.

57. A process in accordance with claim 56 wherein the toner particles obtained are coated with surface release components.

58. A process in accordance with claim 56 wherein the toner particles obtained are coated with conductive components.

59. A process in accordance with claim 56 wherein the shell forming interfacial polycondensation is accomplished by heating.

60. A highlight colored encapsulated toner comprised of the components of claim 1.

61. An encapsulated toner composition comprised of a core comprised of a polymer resin, color pigment, excluding black, a lightly colored magnetic material, and a whitening agent.

62. An encapsulated toner composition comprised of a core comprised of polymer resin particles, color pigment particles, colorless or lightly colored magnetic material particles, and whitening agent particles, and which core is encapsulated in a polymeric shell, and wherein the shell has optionally incorporated therein on the shell surface or within the shell polymer functional additives comprised of conductive components and release agents.

63. A highlight colored encapsulated toner comprised of a core comprised of a polymer resin, color pigment, excluding black, a substantially colorless or lightly colored magnetic material, and a whitening agent.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 10 9145

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	EP-A-0 362 859 (CANON K.K.) * Claims * – – –	1-63	G 03 G 9/093
A	PATENT ABSTRACTS OF JAPAN, vol. 12, no. 422 (P-783)[3269], 9th November 1988; & JP-A-63 157 167 (FUJI PHOTO FILM CO.) 30-06-1988 * The whole abstract * – – –	1-63	
A	PATENT ABSTRACTS OF JAPAN, vol. 12, no. 359 (P-762)[3206], 27th September 1988; & JP-A-63 110 459 (MATSUSHITA ELECTRIC IND. CO.) 14-05-1988 * The whole document * – – –	1-63	
A	US-A-4 851 318 (HSIEH et al.) * Claims; columns 10-11; example 1 * – – –	1-63	
A	PATENT ABSTRACTS OF JAPAN, vol. 13, no. 377 (P-922)[3725], 22nd August 1989; & JP-A-1 131 574 (TOPPAN PRINTING CO., LTD) 24-05-1989 * Whole document * – – –	1-63	**TECHNICAL FIELDS SEARCHED (Int. Cl.5)**
A	DATABASE WPIL, accession no. 89-195264 [27], Derwent Publications Ltd, London, GB; & JP-A-1 131 574 (TOPPAN PRINTING) – – – – –	1-63	G 03 G

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	27 August 91	HILLEBRECHT D.A.O.

CATEGORY OF CITED DOCUMENTS

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