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(54) Dry electrostatographic toner particles.

(57) A dry electrostatographic toner composition is provided having toner particles comprising at least one organic colouring substance, at least one binder resin and at least one inorganic filler material, characterised in that

(i) said inorganic filler material is chemically inert towards said binder material, is evenly dispersed throughout the volume of the toner particles and is present in the toner particles in such amounts that said filler material presents a surface of at least 0.5 m^2 pro gram of resinous toner matrix and

(ii) said binder resin is such that the melt viscosity at 120 °C of the resinous matrix containing 1 m^2 surface of said filler material pro gram of resin is, in comparison to the melt viscosity of the same resinous matrix without said filler material, not raised or at most by a factor $f = 1.25$.

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1. Field of the invention.

This invention relates to electrostatographic toners suitable for use in a electrostatic developer, be it two component or monocomponent developers. In particular this invention relates to heat fixable electrostatographic colour toners suitable for use in a full colour printing system .

2. Background of the Invention.

It is well known in the art of electrographic printing and electrophotographic copying to form an electrostatic latent image corresponding to either the original to be copied, or corresponding to digitised data describing an electronically available image.

In electrophotography an electrostatic latent image is formed by the steps of uniformly charging a photoconductive member and imagewise discharging it by an imagewise modulated photo-exposure.

In electrography an electrostatic latent image is formed by imagewise depositing electrically charged particles, e.g. from electron beam or ionized gas onto a dielectric substrate.

The obtained latent images are developed, i.e. converted into visible images by selectively depositing thereon light absorbing particles, called toner particles, which usually are triboelectrically charged.

In toner development of latent electrostatic images two techniques have been applied : "dry" powder and "liquid" dispersion development of which dry powder development is nowadays most frequently used.

In dry development the application of dry toner powder to the substrate carrying the latent electrostatic image may be carried out by different methods known as, "cascade", "magnetic brush", "powder cloud", "impression" or "transfer" development also known as "touchdown" development described e.g. by Thomas L. Thourson in IEEE Transactions on Electronic Devices, Vol. ED-19, No. 4, April 1972, pp.495-511.

In most cases the latent image is developed with a finely divided developing material or toner to form a powder image which is then transferred onto a support sheet such as paper.

The transferred image may subsequently be permanently affixed to the substrate by heat, pressure, or a combination of heat and pressure.

Electrophotographic processes can not only be employed to form monochrome (black) images, but also to form colour images. It is known to form full colour images by sequentially forming and developing electrostatic colour separation images with cyan, magenta, yellow and black toners respectively. In such applications high quality toners are needed.

By 'quality' in electrostatography is generally understood a true, faithful reproduction of the original to be copied, or faithful visual print of the electronically (digitally) available image.

Quality comprises features such as uniform darkness of the image areas, background quality, clear delineation of lines, good resolution of the image and particularly for colour images correct hue, high saturation and high lightness.

It is known that one of important contributing characteristics of high quality electrostatographic toners is the size and size distribution of the developer particles used, and in case a two component developer material is used, in particular the size and size distribution of the toner particles employed. In the document published by ATR Corporation, 6256 Pleasant Valley Road, El Dorado, California 95623, entitled 'Effect of Toner Shape on Image Quality' published March 28, 1988, the influence of toner particle diameter and shape upon image quality, particularly for high resolution images, has been tested. Examples of toners comprising small particles with a narrow size distribution are disclosed in e.g. US P 4,748,474 ; US P 4,737,433 ; US P 4,434,220 ; US P 4,822,060 and WO A1 91/00548.

For use in full-colour electrophotography each of the colour toners should present a high degree of colour mixing. When using electro(photo)graphy in "graphical" applications, i.e. in applications where the images are used in the printing industry or are compared with images the printing industry is accustomed to, the demands on colour balance and high fidelity rendition of slight differences in hue, saturation and lightness are at their highest. One of the important requirements for the system is that it allows the easy fusing and intimately mixing of two or more toner layers of different colours to yield a faithful rendition of the hues present in the original. A way to achieve this is to use an electr(photo)graphic system that uses a heat fixing step for producing the final image. In that case it is necessary that the full colour density of any colour patch in the image may be reached with as few as possible overlaying toner layers so as to avoid problems with colour mixing in thick layers, with height and/or gloss differences between high density and low density areas. Thus a high colour efficiency, which means a high colour density pro gram toner (pro particle) is a very desirable feature. High colour efficiency is achieved by employing as colourant a dye molecularly dissolved in the toner resin. To achieve high light-fastness however the use of organic colouring pigment particles is preferred in the production of colour toners. Generaly organic colouring pigment particles with an average particle size of about 50 nm or less, are dispersed in the binder resin. The use of such organic colouring pigment particles is preferred notwithstanding the great efforts needed to finely and evenly disperse said particles in the binder resin.

Fine and even dispersion of the pigment is necessary not only because a bad dispersion influences negatively the quality of the toner particles as such (e.g. due to different pigment load of the individual toner particles uneven charge distribution, colour deviations within individual toner particles, uneven melt characteristics etc.), but also because it will be necessary to add more pigment to achieve the desired density (increasing the cost of the toner) or more toner particles are to be deposited one over another to give the desired colour density in the final image (raising problems as to the melt energy that has to be delivered in a heat fixing process and the problems with height and/or gloss-differences between high density and low density areas).

The problem of finely and evenly dividing the pigment or dye in an electrographic toner has been addressed in various ways.

In US P 5,102,763 it is described to use hydrophilic silica particles having dyes covalently bonded to the particle surfaces through silane coupling agents and a polymer having at least one segment capable of adsorbing onto the surface of the silica particles and at least one segment capable of enhancing the dispersability of the silica particles in the toner resin.

In US-P 5,080,995 a process for enabling effective toner pigment dispersion is described which comprises dry blending toner resin, pigment and a polymeric alcohol $CH_3(CH_2)_nCH_2OH$ with n from 15 to 300), melt kneading the mixture and classifying the toner particles.

In US-P 5,102,764 the problem is adressed by using a specific dye.

Each of the solutions above has its own merits, but also its drawbacks.

A simple, cost effective way to finely and evenly divide organic colouring pigment particles in toner particles without negatively influencing the properties of the toner particles (e.g. hot offset properties, stability, flowability, easy cleaning of the photconductive member) is still desirable.

3. Objects and Summary of the Invention.

It is an object of the invention to provide toner particles useful for high fidelity electrostatographic colour image reproduction, i.e. for full colour reproduction, yellow, magenta, cyan and black toner particles, which contain finely and evenly divided pigments (e.g. organic colouring pigment) so as to yield a high colour rendering in a heat fixing process, without presenting problems of too high a melt viscosity and lack of definition.

It is another object of the invention to provide yellow, magenta, cyan and black toner particles useful for high fidelity electrostatographic colour reproduction with which it is possible, when used in an electro(stato)-graphic system comprising a heat fixing step, to deliver a full colour image with an image quality that meets the quality standards of offset printing with lithographic printing inks.

Further objects and advantages of the present ivention will become clear from the detailed description hereinafter.

The above objects are accomplished by providing a dry electrostatographic toner composition having toner particles comprising at least one organic colouring substance, at least one binder resin and at least one inorganic filler material, characterised in that

(i) said inorganic filler material is chemically inert towards said binder material, is evenly dispersed throughout the volume of the toner particles and is present in the toner particles in such amounts that said filler material presents a surface of at least 0.5 m^2 pro gram of resinous toner matrix and

(ii) said binder resin is such that the melt viscosity at 120 °C of the resinous matrix containing 1 m^2 surface of said filler material pro gram of resin is, in comparison to the melt viscosity of the same resinous matrix without said filler material, not raised or at most by a factor $f = 1.25$.

4. Detailled Description.

According to the present invention, the dispersion of organic colouring pigment particles in a toner resin is greatly facilitated and the tendency of the pigment particles for agglomeration greatly reduced when during the melt kneading step of the toner production inorganic filler materials are present.

The incorporation of inorganic fillers in the bulk of toner particles is known.

It is known from Japanese Unexamined Application JP 60/103,356 that the addition of an inorganic filler to the core of encapsulated toner particles is advantageous to improve the mechanical strenght of the toner particles intended for use in development processes that use a cold pressure fixing step.

In EP 078,077 a water fixable toner containing inorganic, water insoluble fillers is disclosed in order to have a toner that can be fixed without requiring a strictly controlled amount of water.

In the Japanese Unexamined Application JP 02/022668, the addition of an inorganic filler to the bulk of the toner particle is disclosed to raise the melt viscosity of tonerparticles for use in a flash fixing process.

The incorporation of inorganic filler material in the bulk of toner particles intended for use in an development process employing a heat fixing step has been disclosed in order to have silica particles at the surface of the toner particles (e.g. JP 18995/1969).

In US P 5,066,558 it is teached that the addition of silica to the bulk of the toner particles to improve flowability poses problems in the heat fixing step of the electrographic proces. This is due to the fact that such an amount of silica is needed, to have enough silica particles at the surface of the toner particle to effectively improve the flowability, that the melt viscosity is raised to unacceptable values. To overcome these problems the patent teaches a process to use silica particles which are only fixed to the surface of the toner particles.

The use of toner particles wherein the pigments are dispersed by the addition of an inorganic filler in electrographic process using a heat fixing step (e.g. by infrared radiation) seems, according to the prior art, impossible since the addition of the inorganic filler increases the melt viscosity of the toner particles to an unacceptable level.

It was found that by using a combination of inorganic filler materials which have basically no chemical reactivity towards the toner resin(s) and by chosing the couple resin/filler such that the melt viscosity at 120 °C of the resinous matrix containing 1 m^2 surface of said filler material(s) pro gram of resin(s) is, in comparison to the melt viscosity of the same resinous matrix without any of said filler material(s), not raised or at most by a factor f of 1.25, it was possible to combine the advantage of an easy procedure to disperse the organic colouring pigment particles in the toner mass and the desired melt viscosity of the toner powder. It has been proven that preferably the melt viscosity at 120 °C of said resinous toner matrix containing 1 m^2 surface of said filler material(s) pro gram of resin(s) is, in comparison to the melt viscosity of the same resinous toner matrix without any of said filler material(s), not raised or is raised by a factor f of at most 1.1.

The low interaction between the inorganic filler material(s) and the binder resin(s) making up the resinous toner matrix is not only beneficial in limiting the raise of melt viscosity of the resinous matrix comprising said inorganic filler materials, but is also beneficial in enhancing the dispersability of the organic colouring pigment particles in the toner mass. It is believed, without however being bound by any theory, that the inorganic filler material has to have enough free and active surface in such a way that the organic colouring substance(s) can interact with the inorganic filler material and be dispersed troughout the toner particles together with the inorganic filler material.

By inorganic filler material is, according to the present invention to be understood any filler being composed of more than 90 % of pure inorganic material. Small organic alterations, such as e.g. those to inhibit moisture degradation of the filler, can be incorporated, as long as the surface activity of the inorganic filler is not completely altered by said small organic alteration.

The inorganic filler material, that, according to the present invention, is incorporated in the bulk of toner particles useful for high fidelity electrostatographic colour reproduction and to be used in an electro(stato)-graphic system comprising a heat fixing step, has to be colourless and transparent. The use of spherical, inorganic filler particles has proved to offer advantages over non spherical particles.

Advantageously spherical fumed inorganics of the metal oxide class, selected from the group consisting of silica (SiO_2) and alumina (Al_2O_3) or mixed oxides thereof are selected. The fumed metal oxide particles have a smooth, substantially spherical surface. Their specific surface area is preferably in the range of 20 to 400 m^2/g, more preferably in the range of 50 to 200 m^2/g. The specific surface area (BET surface) can be measured by a method described by Nelsen and Eggertsen in "Determination of Surface Area Adsorption measurements by continuous Flow Method", Analytical Chemistry, Vol. 30, No. 9 (1958) p. 1387-1390.

It is possible to use either hydrophobic or hydrophilic inorganic particles to disperse an organic colourant in the toner particles according to the present invention, on the condition that the inorganic filler particles are chemically non-reactive towards the binder resin(s) and that the melt viscosity at 120 °C of the resinous matrix containing 1 m^2 surface of said inorganic filler paricles pro gram of resin(s) is, in comparison to the melt viscosity of the same resinous matrix without any of said filler material(s), not raised or at most by a factor f of 1.25

In preferred embodiments the proportions for fumed metal oxides such as silica (SiO_2) and alumina (Al_2O_3) incorporated in the particle composition of the toner particles are in the range of 3 to 30 % by weight.

The toner particles used in accordance with the present invention may comprise any conventional resin binder. The binder resins used for producing toner particles according to the present invention may be addition polymers e.g. polystyrene or homologues, styrene/acrylic copolymers, styrene/methacrylate copolymers, styrene/acrylate/acrylonitile copolymers or mixtures thereof. Addition polymers suitable for the use as a binder resin in the production of toner particles according to the present invention are disclosed e.g. in BE 61.855/70, DE 2,352,604, DE 2,506,086, US-P 3,740,334.

Also polycondensation polymers may be used in the production of toner particles according to the present invention. Polyesters prepared by reacting organic carboxylic acids (di or tricarboxylic acids) with polyols (di- or triol) are the most prefered polycondensation polymers. The carboxylic acid may be e.g. maleic acid, fumaric acid, phthalic acid, isophthalic acid, terephthalic acid, trimellitic acid, etc or mixtures thereof. The polyolcomponent may be ethyleneglycol, diethylene glycol, polyethylene glycol, a bisphenol such as 2,2-bis(4-hydroxyphenyl)-propane called "bisphenol A" or an alkoxylated bisphenol, a trihydroxy alcohol, etc or mixtures thereof. Polyesters, suitable for use in the preparation of toner particles according to the present invention are disclosed in e.g. US-P 3,590,000, US-P 3,681,106, US-P 4,525,445, US-P 4,657,837, US-P 5,153,301.

It is also possible to use a blend of additionpolymers and polycondensation polymers in the preparation of toner particles according to the present invention as disclosed e.g. in US-P 4,271,249.

The inorganic filler material according to the present invention can be added to yellow, magenta and cyan toners to enhance the dispersability of the organic colouring pigment particles in the toner particles.

When, for producing black toner particles the colourant is a mixture of at least three organic colouring pigments (yellow, magenta and cyan) to ensure a neutral grey (black) colour, it is advantageous to use filler material according to the present invention. Neutral black means that the black colour absorbs the light of the visible spectrum in an amount that is independent of the wavelenght. It is also possible to combine (an) organic colouring pigment(s) (e.g. a cyan dye) with an inorganic black pigment to ensure that the black toner will yield a neutral black colour. Preferably the inorganic black pigment, used together with an organic colouring pigment to have a neutral black, is carbon black. Examples of carbon black are lamp black, channel black and furnace black e.g. SPEZIALSCHWARZ IV (trade name of Degussa Frankfurt/M - Germany) and VULCAN XC 72 and CABOT REGAL 400 (trade names of Cabot Corp. High Street 125, Boston, U.S.A.).

The colour toners (yellow, magenta and cyan) may contain organic colouring pigments of the group of phthalocyanine dyes, quinacridone dyes, triaryl methane dyes, sulphur dyes, acridine dyes, azo dyes and fluoresceine dyes. A review of these colouring substances can be found in "Organic Chemistry" by Paul Karrer, Elsevier Publishing Company, Inc. New York, U.S.A (1950).

Likewise may be used the colouring substances described in the following published European patent applications (EP-A) 0 384 040, 0 393 252, 0 400 706, 0 384 990, and 0 394 563.

It is possible, when necessary for fine tuning the hue, chroma and lightness of the colour of the toner particles, to add to the toner composition, according to the present invention, soluble dyes together with said organic colouring pigments.

Examples of particularly suited organic colouring substances are listed according to their colour yellow, magenta or cyan and are identified by name and Colour Index number (C.I. number) in the following Table 1 which also refers to the manufacturer.

TABLE 1

Yellow dye	Colour Index 1 and 2		Manufacturer
Permanent Yellow GR	PY 13	21100	Hoechst AG
Permanent Yellow GG02	PY 17	21105	id
Novoperm Yellow FGL	PY 97	11767	id
Permanent Yellow GGR	PY 106		id
Permanent Yellow GRY80	PY 174		id
Sicoechtgelb D1155	PY 185		BASF
Sicoechtgelb D1350DD	PY 13	21100	id
Sicoechtgelb D1351	PY 13	21100	id
Sicoechtgelb D1355DD	PY 13	21100	id
Magenta dye			
Permanent Rubin LGB	PR57:1	15850:1	Hoechst AG
Hostaperm Pink E	PR122	73915	id
Permanent Rubin E02	PR122	73915	id
Permanent Carmijn FBB02	PR146	12433	id
Lithol Rubin D4560	PR57:1	15850:1	BASF
Lithol Rubin D4580	PR57:1	15850:1	id
Lithol Rubin D4650	PR57:1	15850:1	id
Fanal Rosa D4830	PR81	45160:1	id
Cyan dye			
Hostaperm Blue B26B	PB15:3	74160 1	Hoechst AG
Heliogen Blau D7070DD	PB15:3	74160	BASF
Heliogen Blau D7072DD	PB15:3	74160	BASF
Heliogen Blau D7084DD	PB15:3	74160	id
Heliogen Blau D7086DD	PB15:3	74160	id

In order to obtain toner particles with sufficient optical density in the spectral absorption region of the colourant, the colourant is preferably present therein in an amount of at least 0.5 % by weight with respect to the total toner composition, more preferably in an amount of 1 to 10 % by weight.

In order to modify or improve the triboelectric chargeability in either negative or positive direction the toner particles may contain (a) charge control agent(s). For example, in published German patent application (DE-OS) 3,022,333 charge control agents for yielding negatively chargeable toners are described. In DE-OS 2,362,410 and US-P 4,263,389 and 4,264,702 charge control agents for positive chargeability are described. Very useful charge controlling agents for providing a net positive charge to the toner particles are described in US-P 4,525,445, more particularly BONTRON NO4 (trade name of Oriental Chemical Industries - Japan) being a nigrosine dye base neutralized with acid to form a nigrosine salt, which is used e.g. in an amount up to 5 % by weight with respect to the toner particle composition. A charge control agent suitable for use in coloured toner particles is zinc benzoate and reference therefor is made to published European patent Application 0 463 876 decribing zinc benzoate compounds as charge controlling agents. Such charge controlling agent may be present in an amount up to 5 % by weight with respect to the toner particle composition.

The toner powder particles according to the present invention may be prepared by mixing the above defined binder resin(s) and ingredients (i.e. organic colouring substance, inorganic filler, etc) in the melt phase, e.g. using a kneader. The kneaded mass has preferably a temperature in the range of 90 to 140 °C, and more preferably in the range of 105 to 120 °C. After cooling the solidified mass is crushed, e.g. in a hammer mill and the obtained coarse particles further broken e.g. by a jet mill to obtain sufficiently .small particles from which a desired fraction can be separated by sieving, wind classification, cyclone separation or other classifying technique. The actually used toner particles have preferably an average diameter between 3 and 20 µm on volume, more preferably between 5 and 10 µm when measured with a COULTER COUNTER (registered trade mark) MULTIZISER particle size analyzer operating according to the principles of electrolyt displacement in narrow aperture and marketed by COULTER ELECTRONICS Corp. Northwell Drive, Luton, Bedfordshire, LC 33, UK. In said apparatus particles suspended in an electrolyte (e.g. aqueous sodium chloride) are forced through a small aperture, across which an electric current path has been established. The particles passing one-by-one each displace electrolyte in the aperture producing a pulse equal the displaced volume of electrolyte. Thus particle volume response is the basis for said measurement.

Suitable milling and air classification may be obtained when employing a combination apparatus such as the Alpine Fliessbeth-Gegenstrahlmühle (A.F.G.) type 100 as milling means and the Alpine Turboplex Windsichter (A.T.P.) type 50 G.C as air classification means, available from Alpine Process Technology, Ltd., Rivington Road, Whitehouse, Industrial Estate, Runcorn, Cheshire, UK. Another useful apparatus for said purpose is the Alpine Multiplex Zick-Zack Sichter also available from the last mentioned company.

The toner particles according to the present invention may also be prepared by a "polymer suspension" process. In this process the resin is dissolved in a water immiscible solvent with low boiling point and the pigment and the inorganic filler are dispersed in that solution. The resulting solution/dispersion is dispersed in an aqueous medium that contains a stabilizer, the organic solvent is evaporated and and the resulting particles are dried. As suspension stabilizer it is possible to use e.g. silica particles, water soluble organic protective colloids (e.g. polyvinylalcohol), surface active agents, etc.

In order to improve the flowability of the toner particles spacing particles may be added externally to said toner particles.

Said spacing particles may be embedded in the surface of the toner particles or protruding therefrom or may be externally mixed with the toner particles, i.e. are used in admixture with the bulk of toner particles after the toner particles are produced. These flow improving additives are preferably extremely finely divided inorganic or organic materials the primary (i.e. non-clustered) particle size of which is less than 50 nm; essentially the same inorganic materials as those used in the preparation step of the toner particles are preferred, but the particles are preferentially hydrophobic. Silica particles that have been made hydrophobic by treatment with organic fluorine compounds for use in combination with toner particles are described in published EP-A 467439.

In preferred embodiments the proportions for fumed metal oxides such as silica (SiO_2) and alumina (Al_2O_3) to be admixed externally to the toner particles, prepared according to the present invention, are in the range of 0.1 to 10 % by weight in respect to the toner particles.

Fumed silica particles are commercially available under the tradenames AEROSIL and CAB-O-Sil being trade names of Degussa, Franfurt/M Germany and Cabot Corp. Oxides Division, Boston, Mass., U.S.A. respectively. For example, AEROSIL R972 (tradename) is used which is a fumed hydrophobic silica having a specific surface area of 110 m^2/g. The specific surface area can be measured by a method described by Nelsen and Eggertsen in "Determination of Surface Area Adsorption measurements by continuous Flow Method", Analytical Chemistry, Vol. 30, No. 9 (1958) p. 1387-1390.

In addition to the fumed metal oxide, a metal soap e.g. zinc stearate, as described in the United Kingdom Patent Specification No. 1,379,252, wherein also reference is made to the use of fluor containing polymer particles of sub-micron size as flow improving agents, may be present in the developer composition comprising the toner particles according to the present invention.

The powder toner particles according to the present invention may be used as mono-component developer, i.e. in the absense of carrier particles but are preferably used in a two-component system comprising carrier particles.

When used in admixture with carrier particles, 2 to 10 % by weight of toner particles is present in the whole developer composition. Proper mixing with the carrier particles may be obtained in a tumble mixer.

Suitable carrier particles for use in cascade or magnetic brush development are described e.g. in United Kingdom Patent Specification 1,438,110. For magnetic brush development the carrier particles may be on the basis of ferromagnetic material e.g. steel, nickel, iron beads, ferrites and the like or mixtures thereof. The ferromagnetic particles may be coated with a resinous envelope or are present in a resin binder mass as described e.g. in US-P 4,600,675. The average particle size of the carrier particles is preferably in the range of 20 to 300 µm and more preferably in the range of 30 to 100 µm.

In a particularly interesting embodiment iron carrier beads of a diameter in the range of 50 to 200 µm coated with a thin skin of iron oxide are used. Carrier particles with spherical shape can be prepared according to a process described in United Kingdom Patent Specification 1,174,571.

In the following examples and comparative (non-invention) examples the properties of the toner particles are measured according to the methods described below.

MEASUREMENT METHODS

MELT VISCOSITY : TEST I

For determining the melt viscosity of the selected sample a RHEOMETRICS dynamic rheometer, RVEM-200 (One Possumtown Road, Piscataway, NJ 08854 USA) is used. The viscosity measurement is carried out at a sample temperature of 120 °C. The sample having a weight of 0.75 g is applied in the measuring gap (about 1.5 mm) between two parallel plates of 20 mm diameter one of which is oscillating about its vertical axis at 100 rad/sec and amplitude of 10^{-3} radians. Before recording the measurement signals which are expressed in poise (P) the sample is allowed to attain thermal equilibrium for 10 minutes.

DIFFERENCE BETWEEN MELTVISCOSITY OF THE RESIN(S) WITH AND WITHOUT INORGANIC FILLER(S) (TEST II)

The meltviscosity increase factor (f) was determined by measuring the melt viscosity of the pure resinous matrix according to test I, which gives the value of η_r in P. The meltviscosity of the resinous matrix to which is added 10 % w/w of inorganic filler material is measured according to test I, yielding a value for η_f in P.
The meltviscosity factor f is determined by

$$f = \left(\frac{\eta_f}{\eta_r} \right)^{(10/BET)}$$

BET is the specific surface of the inorganic filler material particles, measured by a method described by Nelsen and Eggertsen in "Determination of Surface Area Adsorption measurements by continuous Flow Method", Analytical Chemistry, Vol. 30, No. 9 (1958) p. 1387-1390 and expressed in m^2/g.

The formula above normalizes the meltviscosity increase factor f to the addition of such an amount of inorganic filler material that the resinous matrix contains 1 m^2 of filler surface pro 1 g of resinous matrix.

DISPERSION ANALYSIS , MICROSCOPIC : TEST III

The material to be tested is heated to 200° C for 15 minutes and diluted with toner resin so as to obtain a final pigment concentration of 1 % w/w in respect to the toner/resin mixture. From the melt a drop is placed on a dust- and fatfree microscopic glass plate. The microscopic glass plate and the molten sample are allowed to equilibrate at 150° C. Then an aluminium foil, 15 µm thick, is applied at two sides of the drop and the drop is drawn to a layer of 15 µm thick by sliding a sharp knife over the aluminium spacer guides. After cooling to room temperature, the sample is observed by a microscope with magnification 100 x or 200 x and photographed. Visual comparison of photographs makes it possible to assess the relative degree of dispersion of the pigment.

DISPERSION ANALYSIS , SPECTROPHOTMETRIC : TEST IV

A predefined amount of the sample to be tested, (0.5 g for toner particles, 0.2 g for masterbatch) is brought into 75 ml dichloromethane and ultrasonically stirred for 30 minutes. After cooling to room temperature the mixture, which is a dispersion of the pigment in dichloromethane, is brought to exactly 100 ml. After further dilution (5 times for toner, 20 times for masterbatch) the absorption of the solution/dispersion is measured in a double beam spectrophotometer. The measurement proceeds with the wavelength of maximal absorption of the pigment under investigation.

Depending on the degree of dispersion of the pigment in the toner resin, the dispersion in dichloromethane absorbs more or less light. The higher the degree of dispersion, the higher the absorption. The density of the dichloromethane dispersion is taken as a measure for the degree of dispersion. The higher the density the better the dispersion.

EXAMPLE 1

In this example the meltviscosity increase factor (f), measured according to test II, for different inorganic filler materials and two different resinous matrices (RESIN A and RESIN B)is presented together with the degree of dispersion of HELIOGEN BLAU (see table 1) measured according to test IV and expressed as absorbance at 640 nm.

Resinous matrix A (RESIN A) consists of a 50/50 polyester blend of (i) a linear polyester of fumaric acid and propoxylated bisphenol A (Mn = 4300, Mw = 14000, acid value = 14) and (ii) a linear polyester of phthalic acid, isophathalic acid, ethylene glycol and ethoxylated bisphenol A (Mn = 3300, Mw = 12000, acid value = 19). Resinous matrix A, without filler material, showed a melt viscosity η of 2900 P. The values of f for resinous matrix A and various inorganic filler materials are to be found in table 2.

Resinous matrix B (RESIN B) is a typical addition polymer for use in the preparation of toner particles, it is a copolymer of styrene and n-Butylmethacrylate and consists of 65 % w/w of styrene and 35 % w/w of n-Butylmethacrylate (Mn = 13200, Mw = 33000). Resinous matrix B, without filler material, showed a melt viscosity η of 17400 P. The values of f for resinous matrix B and inorganic filler materials are to be found in table 3.

TABLE 2

Filler	BET in m^2/g	Hydrophilic/hydrophobic	f	Absorbance at 640 nm
none	-	-	1	0.94
Al_2O_3	150	Hydrophilic	1.06	1.55
SiO_2 *	160	Hydrophobic	1.06	1.51
SiO_2 **	42	Hydrophobic	1.28	1.14
SiO_2 ***	113	Hydrophobic	1.05	1.36
$CaCO_3$	20	Hydrophobic	1.50	1.25
TiO_2	50	Hydrophilic	1.13	1.60

* fumed spherical silica sold under tradename R504 by Degussa AG, Germany

** precipitated spherical silica sold under tradename NIPSIL SS70 by Nippon Silica Ind., Japan

*** precipitated spherical silica sold under tradename NIPSIL SS20 by Nippon Silica Ind., Japan.

TABLE 3

Filler	BET in m^2/g	Hydrophilic/hydrophobic	f	Absorbance at 640 nm
none	-	-	1	1.19
Al_2O_3	150	Hydrophilic	1.02	1.37
$CaCO_3$	20	Hydrophobic	1.09	1.34

From table 2 and 3 it becomes clear that a low interaction between the resinous matrix and the inorganic filler materials goes together with an high degree of dispersion. It is striking that $CaCO_3$ is an inapropriate inorganic filler when used with resinous matrix A and is a very acceptable inorganic filler when used with resinous matrix B. It becomes also clear that $f \leqq 1.25$ is advantageous for the dispersability of the organic colouring substance.

In the following examples and comparative (non-invention) examples, the dispersion of various colourants in the toner particles with the use of inorganic fillers according to the present invention is illustrated and visually inspected using test III and quantified using test IV.

EXAMPLE 2

RESIN A, 77 parts by weight, 20 parts by weight of Al_2O_3C (ALUMINIUMOXIDE C, a tradename of Degussa AG, Frankfurt, Germany for hydrophilic aluminiumoxide with BET surface of 100 m^2/g) and 3 parts by weight of Heliogen Blau (table 1) are intimately mixed together, melt kneaded, crushed and classified to give toner particles with average particle size of 8.5 μm based on volume.

COMPARATIVE EXAMPLE 1

The procedure of example 2 was repeated exept for the fact that 97 parts by weight of the polyester binder (RESIN A) was used and no aluminiumoxide C was present.

The degree of dispersion of the pigment was evaluated for both example 2 and comparative example 1 according to test III and test IV. The results are shown in table 4.

TABLE 4

	Test III Microscopic test	Test IV Absorbance at 640 nm
Example 2	No agglomarates	1.44
Comparative example 1	Agglomerates	0.87

EXAMPLES 3 to 8.

Six cyan toners as in example 2 were prepared, with varying concentrations of aluminiumoxide C (examples 3 to 7). When producing cyan toner as in example 1, 10 % w/w of silica R504 (tradename of Degussa AG, Frankfurt Germany for fumed silica with BET = 160 m^2/g) was added instead of aluminium oxide C (example 8). The resulting toners were evaluated according to test IV. The results are shown in table 5.

TABLE 5

	Test IV : absorbance at 640 nm
Comparative ex 1 0 Al_2O_3 C (% w/w)	0.83
ex 3 1 Al_2O_3 C (% w/w)	0.92
ex 4 2 Al_2O_3 C (% w/w)	1.14
ex 5 5 Al_2O_3 C (% w/w)	1.45
ex 6 10 Al_2O_3 C (% w/w)	1.61
ex 7 20 Al_2O_3 C (% w/w)	1.61
ex 8 10 SiO_2 (% w/w)	1.52

EXAMPLE 9

Toner particles were produced by intimatly mixing 85 % w/w of RESIN A, 5 % w/w of Sicoechtgelb (table 1), 10 % w/w of aluminium oxide C, melt kneading the mixture, cooling, crushing and classifying to obtain toner particles with average particle size of 8.30 μm based on volume.

COMPARATIVE EXAMPLE 2

The procedure of example 9 was repeated, except that 95 % w/w of toner resin was present and no aluminiumoxide C.

The dispersion quality of the pigment in both toners was evaluated according to test IV. The results are to be found in table 6.

TABLE 6

	Test IV : Absorbance at 485 nm
Example 9	2.06
Compartive example 2	1.79

EXAMPLE 10

Toner particles were produced by intimatly mixing 84.75 % w/w of RESIN A, 2.25 % w/w of Hostaperm Rosa E (table 1), 2.75 % w/w of Permanent Carmine FBB02 (table 1), 10 % w/w of aluminium oxide C, melt kneading the mixture, cooling, crushing and classifying to obtain toner particles with average particle size of 8.35 µm.

COMPARATIVE EXAMPLE 3

The procedure of example 10 was repeated, except that 95 % w/w of toner resin was present and no aluminiumoxide C.

The dispersion quality of the pigment in both toners was evaluated according to test IV. The results are to be found in table 7.

TABLE 7

	Test IV : Absorbance at 537 nm
Example 10	1.54
Compartive example 3	0.99

Claims

1. A dry electrostatographic toner composition having toner particles comprising at least one organic colouring substance, at least one binder resin and at least one inorganic filler material, characterised in that

(i) said inorganic filler material is chemically inert towards said binder material, is evenly dispersed throughout the volume of the toner particles and is present in the toner particles in such amounts that said filler material presents a surface of at least 0.5 m^2 pro gram of resinous toner matrix and

(ii) said binder resin is such that the melt viscosity at 120 °C of the resinous matrix containing 1 m^2 surface of said filler material pro gram of resin is, in comparison to the melt viscosity of the same resinous matrix without said filler material, not raised or at most by a factor $f = 1.25$.

2. A dry electrostatographic toner composition according to claim 1, wherein the melt viscosity at 120 °C of the resinous matrix containing 1 m^2 surface of said filler material(s) pro gram of resin(s) is, in comparison to the melt viscosity of the same resinous matrix without any of said filler material(s), not raised or is raised by a factor f of at most 1.10.

3. A dry electrostatographic toner composition according to claim 1 or 2, wherein said filler material is present in an amount of 3 to 30 % by weight as compared to the resin(s).

4. A dry electrostatographic toner composition according to any of the preceding claims, wherein said inorganic filler material comprises silica and/or alumina.

5. A dry electrostatographic toner composition according to claim 4, wherein said inorganic filler material comprises fumed silica and/or alumina.

6. A dry electrostatographic toner composition according to any of the preceding claims, wherein said filler material consists of spherical particles.

7. A dry electrostatographic toner composition according to any of the preceding claims, wherein the surface of said filler material is hydrophilic.

8. A dry electrostatographic toner composition according to any of the preceding claims, wherein said filler material has a BET surface of at least 20 m^2/g.

9. A dry electrostatographic toner composition according to any of the preceding claims, wherein said binder resin comprises a polyester.

10. A Dry electrostatographic toner particles according to claim 9, wherein said polyester is a linear polyester or a blend of polyesters.

11. A dry electrostatographic toner compositon according to any of claims 1 to 8, wherein said binder resin comprises an addition polymer comprising styrene and/or acrylic moieties and/or methacrylic moieties.

12. A dry electrostatographic toner composition according to claim 11, wherein said addition polymer is a linear addition polymer or a blend of addition polymers.

13. A dry electrostatographic toner composition according to any of claims 1 to 8, wherein said binder resin comprises a blend of a polyester and an addition polymer.

14. A dry electrostatographic toner composition according to any of the preceding claims, wherein said organic colouring substance(s) are Yellow, Magenta, Cyan colouring substances or a mixture thereof and wherein the toner mass has a melt viscosity at 120 °C between 2500 and 15000 P.

15. Use of a dry electrostatographic toner composition according to any of the preceding claims in an electrostatographic process that comprises a non contact heat fusing step.

16. Use of a dry electrostatographic toner composition according to any of claims claims 1 to 14 in an electrostatographic process that uses a monocomponent electrostatographic developer.

17. Use of a dry electrostatographic toner composition according to any of claims 1 to 14 in an electrostatographic process that uses a two component electrostatographic developer comprising developer and toner particles.

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 93 20 1647

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)
D,A	PATENT ABSTRACTS OF JAPAN vol. 14, no. 167 (P-1031)30 March 1990 & JP-A-02 022 668 (FUJITSU LTD.) 25 January 1990 * abstract * ---	1-17	G03G9/097
A	DE-A-27 08 061 (RICOH CO., LTD.) * claims 1-4 * ---	1-17	
A	EP-A-0 037 297 (COMPAGNIE INTERNATIONALE POUR L'INFORMATIQUE CII - HONEYWELL BULL) * page 14, line 29 - line 36; claim 1 * -----	1	

TECHNICAL FIELDS SEARCHED (Int.Cl.5)
G03G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	22 October 1993	HINDIA, E

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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