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(54) ELECTROSTATICALLY AND/OR MAGNETICALLY ATTRACTABLE TONER POWDER

TONERPULVER, DAS ELEKTROSTATISCH UND/ODER MAGNETISCH ANGEZOGEN WIRD

POUDRE TONER ATTIRABLE DE MANIERE ELECTROSTATIQUE ET/OU MAGNETIQUE

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- **PATENT ABSTRACTS OF JAPAN vol. 9, no. 16 (P-329) (1739) 23 January 1985 & JP,A,59 164 560**
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Description

1. Field of the invention.

The present invention relates to a toner composition suited for development of electrostatic charge images or magnetic patterns.

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 digitized 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 (plasma) 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 magnetography a latent magnetic image is formed in a magnetizable substrate by a patternwise modulated magnetic field. The magnetizable substrate must accept and hold the magnetic field pattern required for toner development which proceeds with magnetically attractable toner particles.

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.

The visible image of electrostatically or magnetically attracted toner particles is not permanent and has to be fixed by causing the toner particles to adhere to the final substrate by softening or fusing them followed by cooling. Normally fixing proceeds on more or less porous paper by causing or forcing the softened or fused toner mass to penetrate into the surface irregularities of the paper.

Dry-development toners essentially comprise a thermoplastic binder consisting of a thermoplastic resin or mixture of resins (ref. e.g. US-P 4,271,249) including colouring matter, e.g. carbon black or finely dispersed dye pigments. The triboelectrically chargeability is defined by said substances and may be modified with a charge controlling agent.

In the low density parts of the electrostatographic or magnetographic toner-developed prints the toner particles are deposited at low coverage and do not form a closed or solid deposit of black or coloured material. On the contrary, in the high density portions toner particles are piled on each other and co-fused to form a closed toner-crust which optically has a quite different look as the separately fixed toner particles in the low density portions. Separately deposited and fixed toner particles or small clusters thereof give rise to a light-straying effect. In particular by inspecting the copy with light directed thereto at small grazing angle the small density parts show a mat (dull) appearance. On the contrary, in the high density parts containing smooth coherently co-fused toner particles light is reflected by the glossy surface of the toner crust; whereby light-reflection stands in relation to the kind of binder which normally is a relatively hard thermoplastic transparent resin or mixture of resins.

There are different types of processes used for fusing a toner powder image to its final substrate. Some are based upon fixation primarily on fusing by heat, others are based on softening by solvent vapours, or by the application of cold flow at high pressure in ambient conditions of temperature. In the fusing processes based on heat, two major types should be considered, the "non-contact" fusing process and the "contact" fusing process. In the non-contact fusing process there is no direct contact of the toner image with a solid heating body. Such process includes : (1) an oven heating process in which heat is applied to the toner image by hot air over a wide portion of the support sheet, (2) a radiant heating process in which heat is supplied by infrared and/or visible light absorbed in the toner, the light source being e.g. an infrared lamp or flash lamp. In said "radiant" non-contact fusing embodiment radiation such as infrared radiation may be at least partly absorbed in the final support and therefrom by conduction transferred to the thereon deposited toner image(s).

According to a particular embodiment of "non-contact" fusing the heat reaches the non-fixed toner image through its substrate by contacting the support at its side remote from the toner image with a hot body, e.g. hot metallic roller.

Non-contact fusing has the advantage that the non-fixed toner image does not undergo any mechanical distortion and fine image details will not suffer from transfer to a contacting fixing member, by so-called "offset" phenomena typical for hot pressure roller fusing.

In an embodiment of common "contact" fusing the support carrying the non-fixed toner image is conveyed through the nip formed by a heating roller also called fuser roller and another roller backing the support and functioning as pressure exerting roller, called pressure roller. This roller may be heated to some extent so as to avoid strong loss of heat within the copying cycle.

In producing halftone, i.e. screened images, toner-contacting pressure fuser rollers can distort the dot structure of the screened images. Such will be particularly the case when the pressure-fuser roller has no perfect smooth structure and texturizes the obtained image.

Whatever the kind of fixing system the above described phenomenon of unequal gloss between low density parts and high density parts will arise, especially when the final print is on a glossy support.

It is desirable to dispose of a toner which on fixing will give an equal not very glossy aspect whatsoever the optical density of the image parts will be. Fixed toner images having a satin-look are preferred for they give a better legibility in text parts and provide a nice image aspect.

3. Objects and Summary of the Invention

It is an object of the present invention to provide a dry toner wherein the composition of the toner particles is such that the fixed toner image independent of its optical density has the same or almost the same reflection properties.

It is more particularly an object of the present invention to provide a dry toner that after fixing offers a satin-look to the fixed toner image without use of special covering layers for controlling reflection properties.

It is more particularly an object of the present invention to provide such dry toner suited for being fixed to a substrate by non-contact fusing by moderate heating.

Other objects and advantages of the present invention will appear from the further description.

In accordance with the present invention a dry powder toner is provided the particles of which are electrostatically or magnetically attractable and suitable for use in the development of electrostatic charge images or magnetic patterns and wherein the composition of said powder particles includes at least one transparent thermoplastic resin P and at lest one compound Q, said compound Q having a more polar character than said resin P, characterized in that said at least one resin P and said at least one compound Q when after been mixed in molten state followed by solidification form a light-scattering composition that under the measurement conditions of the following test R has a corrected optical absorption value (A_{cor}) as described in said test R of more than 0.10 but not more than 1.0, said resin(s) P and compound (s) Q being present in said toner in a weight ratio range P/Q from 5:1 to 1:5, and the weight ratio of P + Q with respect to the total weight of the toner is equal to or larger than 25:100.

The toner particles according to the present invention normally contain a colorant but may be colourless for obtaining a desired surface aspect.

DESCRIPTION OF TEST R

Resin material P and compound Q are pulverized to a particle size smaller than 1 mm. A powder mixture of P and Q is made taken equal weight amounts of said both ingredients. The powder mixture is fed to a single shaft screw-extruder of bore diameter 19 mm and length 25 times said diameter. The extruder is heated in such a way that the temperture of the extruded product is between 100 and 120 °C at 50 screw revolutions per minute and the molten product is extruded through a slit to form a ribbon having a thickness of about 500 μm.

A part of that ribbon is put on a microscope glass carrier plate and conditioned thereon for 10 minutes at 145 °C. The resultant thickness of the film (about 250 μm) is measured and the optical absorption of the film determined by means of a double beam spectrophotometer type ACTA CIII (tradename of BECKMAN Instruments, Inc., Fullerton, CA 92634 U.S.A.) operating with light of 540 nm.

The measured optical absorption (absorbance) is expressed for a film thickness of 250 μm using the equation :

$$A = Ay/y$$

A = absorbance of a 250 μm thick film.
Ay = measured absorbance of a film of y μm thickness, and
y = thickness of film in μm.

Since the satin-look is a direct result of the internal light-scattering of the obtained mixture and not of the light-absorption due to intrinsic colour of the separate ingredients P and Q, the above optical density measurement was repeated for the separate pure materials P and Q and the obtained density values for said pure materials were subtracted therefrom. A corrected absorption density value (A_{cor}) of the test mixture of P and Q for a same sample thickness is therefore obtained by the following equation :

$$A_{cor} = A_{P+Qmix} - (A_P/2 + A_Q/2)$$

A_{cor} stands for the corrected optical absorption density of the test mixture containing P and Q in a 1/1 weight ratio,
A_{P+Qmix} is the total (uncorrected) optical absorption density of the test mixture containing P and Q in said 1/1 weight ratio,
$A_P/2$ is the optical absorption density of the pure resin P at same layer thickness as for the mixture of P and Q, and
$A_Q/2$ is the optical absorption density of the selected compound Q at same layer thickness as for the mixture of P and Q.

4. Detailed Description of the Invention

The weight ratio of P + Q with respect to the total weight of the toner is prefereably equal to or larger than 75:100. A heat-fixed toner image showing satin-look can be obtained already when said "corrected" optical absorption density value (A_{cor}) for the test mixture of resin(s) P and compound(s) Q is at least 0.1, but preferably said optical density is in the range of 0.3 to 0.7. When said absorption density value exceeds 1.0 the incompatibility of P and Q begins to pose serious problems in that the toner composition becomes too strongly inhomogeneous.

In a preferred dry toner powder according to the present invention said weight ratio range P/Q is 3:1 to 1:3.

It has been found experimentally that a proper fusing is necessary to obtain the desired satin-look effect. When the fusing is poor, the toner images independently of their coverage have an overall mat aspect since the toner particles largely remain separate and not co-fused. Further, by the fact that individual toner particles are insufficiently co-fused and not coalesced colour mixing is poor. The application of heat in excess will result in a good co-fusing of the individual toner particles and gives smooth glossy toner images but such at the expense of image resolution (line spread) and excessive dot gain in halftone (screened) images.

Best results with regard to satin-look are obtained by means of resin(s) P and compound(s) Q that are almost compatible in the molten state and by means of which no substantial phase separation takes place. Phase separation may have a deteriorating effect on cohesiveness and will give rise to the production of toner particles with inhomogeneous character and different electrostatic properties.

So, it is preferred that the resin(s) P and compound(s) Q do not disturb an even distribution of the other toner ingredients such as colouring matter, charge controlling agents, flowing agents, etc.

For use in non-contact fusing said resin(s) P acting as binder in the toner have preferably a glass transition temperature (Tg) larger than 45 °C, and preferably a melt viscosity smaller than 10,000 poise at 120 °C as determined by Test V described furtheron.

A first rough criterion to select a compound Q in combination with a chosen toner resin P is based on the use of the HILDEBRAND solubility parameter for said compound Q with respect to said resin P, that may be a mixture of resins A and B. The notion HILDEBRAND solubility parameter is described in the book "The Solubility of Non-electrolytes" by J.H. Hildebrand and R.L. Scott, Dover Publications, Inc., New York, 3th. ed. (1964).

The desired effect of satin-look of fused and solidified toner may be obtained by mixing polymers being selected in such a way that they have slight incompatibility with respect to each other. The HILDEBRAND parameter solubility for polymers is described in the book "Properties of Polymers" by D.W. Van Krevelen, 2nd. ed., Elseviers Scientific Publishing Company, New York, 1976, Chapter 7.

In general the desired slight incompatibility can be obtained by combining a thermoplastic resin P, e.g. a polyester, with a compound Q having a more polar character than said resin. By more polar character is meant possesing a higher dielectric constant and/or better wettability by water. For example, a water-insoluble polyester is used as resin P in combination with a compound Q including ether units such as ethylene oxide units or amino units such as dialkyl-amino units.

In a preferred dry toner powder according to the present invention said resin P is a polyester derived from an aliphatic dicarboxylic acid and a diol being a propoxylated Bisphenol A.

Examples of particularly useful polymer pairs that fulfil the requirement of slight incompatibility giving rise to the desired satin-look in the fused and thereupon solidified state are a first resin A being a polyester resin with low (less than 5.5 mol/kg) carbonyloxy group (-CO.O-) content (the carbonyloxy groups are part of the ester groups), which resin A is preferably derived from a non-aromatic dicarboxylic acid, e.g. fumaric acid and an ethoxylated and/or propoxylated Bisphenol A, and a second resin B being a polyester with high (at least 7.5 mol/kg) carbonyloxy group content, which resin B is preferably a polyester derived from an aromatic dicarboxylic acid and a diol. The latter polyester is preferably derived from terephthalic acid and isophthalic acid, or mixtures thereof. In the production of said resins B the diol is preferably ethylene glycol optionally mixed with DIANOL 22 and DIANOL 33 as long as the ethylene glycol content of the totality of diols is more than 50 mol %, preferably at least 60 mol %.

A polyester of fumaric acid and DIANOL 33 is marketed under the tradename ATLAC T500 (Tg - 50.5 °C) (ATLAC is a registered trade name of Atlas Chemical Industries Inc. Wilmington, Del. U.S.A.).

DIANOL 22 is di-ethoxylated Bisphenol A.

DIANOL 33 is di-propoxylated Bisphenol A.

Bisphenol A = 4,4'isopropylidenediphenol.

Other useful polymer pairs for obtaining the desired satin-look of the fixed toner are in the group of polymers wherein the above mentioned carbonyloxy groups are wholly or partly replaced by carbonylimine (-CO.NH-) groups, being as the carbonyloxy groups fairly polar groups.

Good satin-look results are obtained likewise by using as polymeric compound P a polyester in combination with a compound Q being a styrene-acrylic resin having a relatively high (more than 70 mol %) styrene content, more particularly copolymers of styrene-acrylic resins or styrene-methacrylic resins, e.g. copoly(styrene/n-butylmethacrylate) or copoly (styrene/2-ethyl-hexylacrylate).

Further good results are obtained by using as polymeric compound P a polyester in combination with a compound Q being a polyether compound, known as CARBOWAX (registered tradename).

Polyester resins suitable for use according to the present invention are selected e.g. from the group of linear polycondensation products of (i) difunctional organic acids, e.g. maleic acid, fumaric acid, terephthalic acid and isophthalic acid and (ii) difunctional alcohols (diol) such as ethylene glycol, triethylene glycol, an aromatic dihydroxy compound, preferably a bisphenol such as 2,2-bis(4-hydroxyphenyl)-propane called "Bisphenol A" or an alkoxylated bisphenol, e.g. propoxylated bisphenol examples of which are given in US-P 4,331,755. For the preparation of suitable polyester resins reference is made to GB-P 1,373,220.

A particularly suitable resin P is a linear polyester of fumaric acid and di-propoxylated bisphenol A, having a melt viscosity of 1800 poise and a Tg of about 50 °C.

Other resins that may be used as compound Q are epoxy resins being a linear adduct of Bisphenol A and epichlorhydrin as described e.g. by D. H. Solomon in the book "The Chemistry of Organic Film Formers" - John Wiley & Sons, Inc, New York (1967) p. 180-181, e.g. EPIKOTE 1004 (EPIKOTE is a registered trade mark of the Shell Chemical Co.) (Tg = 52 °C).

The glass transition temperature (Tg) mentioned herein is determined according to ASTM Designation : D 3418-82.

The melt viscosity mentioned herein is determined by the following test V.

TEST V

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.

Examples of particularly useful polyester resins are listed in the following Table 1, mentioning their glass transition temperature (Tg), melt viscosity, weight-average molecular weight(Mw), number-average molecular weight (Mn), and carbonyloxy content (CC) expressed in (mol/kg).

TABLE 1

Resin	No.	Tg °C	Melt visc. poise	M_w	M_n	CC mol/kg
Polyester A1	1	50.5	1800	14,000	4,500	4.88
Polyester B1	2	65	5500	11,500	3,700	7.19
Polyester C1	3	63	7000	16,000	3,500	8.33
Polyester D1	4	69	16000	25,500	7,100	13.89

Polyester A1 is ATLAC T500 (tradename).

Polyester B1 is an aromatic polyester resin derived from terephthalic acid (100 mol %) as aromatic diacid and a mixture of DIANOL 33 (50 mol %) and ethylene glycol (50 mol %) as diols.

Polyester C1 is an aromatic polyester resin derived from terephthalic acid (40 mol %), isophthalic acid (60 mol %) as aromatic di-acids and a mixture of DIANOL 22 (40 mol %) and ethylene glycol (60 mol %).

Polyester D1 is an aromatic polyester resin derived from terephthalic acid (64 mol %), isophthalic acid (36 mol %)

as aromatic di-acids and ethylene glycol (100 mol %).

According to the above defined test R, A_{cor} values were determined for pairs of resins of the above Table 1. Mixtures of resins 1 and 3 yield an A_{cor} value of 0.50, mixtures of resins 1 and 4 yield an A_{cor} value of 0.53, whereas mixtures of resins 1 and 2 yield an A_{cor} value of 0.017, being not within the claim of the present invention.

Examples of particularly useful styrene copolymers are listed in the following Table 2, mentioning their glass transition temperature (Tg), melt viscosity, weight-average molecular weight (Mw) and number-average molecular weight (Mn).

TABLE 2

Resin	No.	Tg °C	Melt visc. poise	M_w	M_n
S1	1	67	17,000	33,000	13,000
S2	2	68	2,850	6,500	2,000

Resin S1 is a copolymer of styrene and methyl acrylate in a 65/35 molar ratio.
Resin S2 is a terpolymer of styrene, methyl acrylate and dimethylaminoethyl methacrylate in a 87/3/10 molar ratio.

According to the above defined test R resin No. 1 of Table 1 mixed with resin No. 2 of Table 2 yields a A_{cor} value of 0.57, and said resin No. 1 of Table 1 mixed with resin No. 1 of Table 2 yields an A_{cor} value of 0.019 being not within the scope of the present claim.

Examples of suitable monomeric compounds Q are given in the following Table 3.

TABLE 3

Compound Q	Melting point °C
arachidic acid	76.3
stearamide	109.0

These compounds Q are applied preferably in combination with a polyester resin as binder.

Compound Q has not to be an organic compound, inorganic compounds that fulfil the requirements of the above described test R may be used as well. For example, colloidal inorganic fillers in such as colloidal silica, alumina and/or titanium dioxide in minor amounts. However, inorganic fillers may give rise to an undesired high melt viscosity, the need for higher fusing energies and may inhibit a bright color rendition.

For producing visible images the toner powder contains in the resinous binder a colorant which may be black or having a colour of the visible spectrum, not excluding however the presence of mixtures of colorants to produce black or a particular colour.

In the preparation of coloured toner particles a resin blend as defined herein is mixed with said colouring matter which may be dispersed in said blend or dissolved therein forming a solid solution.

In black-and-white copying the colorant is usually an inorganic pigment which is preferably carbon black, but is likewise e.g. black iron (III) oxide. Inorganic coloured pigments are e.g. copper (II) oxide and chromium (III) oxide powder, milori blue, ultramarine cobaltblue and barium permanganate.

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 characteristics of a preferred carbon black are listed in the following Table 4.

TABLE 4

origin	furnace black
density	1.8 g x cm^{-3}
grain size before entering the toner	25 nm
oil number (g of linseed oil adsorbed by 100 g of pigment	70
specific surface (sq.m per g)	96
volatile material (% by weight)	2.5
pH	4.5
colour	black

In order to obtain toner particles having magnetic properties a magnetic or magnetizable material in finely divided

state is added during the toner production.

Materials suitable for said use are e.g. magnetizable metals including iron, cobalt, nickel and various magnetizable oxides, e.g. heamatite (Fe_2O_3), magnetite (Fe_3O_4), CrO_2 and magnetic ferrites, e.g. these derived from zinc, cadmium, barium and manganese. Likewise may be used various magnetic alloys, e.g. permalloys and alloys of cobalt-phosphors, cobalt-nickel and the like or mixtures of these.

Toners for the production of colour images may contain organic colorants that may be dyes soluble in the binder resin or pigments including mixtures thereof. Particularly useful organic colorants are selected from the group consisting of phthalocyanine dyes, quinacridone dyes, triaryl methane dyes, sulphur dyes, acridine dyes, azo dyes and fluoresceine dyes. A review of these dyes can be found in "Organic Chemistry" by Paul Karrer, Elsevier Publishing Company, Inc. New York, U.S.A (1950).

Likewise may be used the dyestuffs 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.

Examples of particularly suited organic dyes 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 5 which also refers to the manufacturer.

TABLE 5

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 colorant, the

colorant is preferably present therein in an amount of at least 1 % by weight with respect to the total toner composition, more preferably in an amount of 1 to 10 % by weight.

Black toner particles according to the present invention for use in fixing by infrared radiant units have preferably a melt viscosity of the powder mass (as defined by test V herein) lower than 7000 P. Colourless toners for use in said fixing unit have preferably a melt viscosity not exceeding 2500 P, and colour toners depending on their radiation absorption have preferably a melt viscosity between 7000 and 3000 P.

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 colourless or 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.

In order to improve the flowability of the toner particles spacing particles may be incorporated therein. Said spacing particles are embedded in the surface of the toner particles or protruding therefrom. 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. Widely used in this context are fumed inorganics of the metal oxide class, e.g. selected from the group consisting of silica (SiO_2), alumina (Al_2O_3), zirconium oxide and titanium dioxide or mixed oxides thereof which have a hydrophilic or hydrophobized surface.

Fumed metal oxides are prepared by high-temperature hydrolysis of the corresponding vaporizable chlorides according to the following reaction scheme illustrative for the preparation of fumed Al_2O_3 :

$$4\ AlCl_3 + 6\ H_2 + 3\ O_2 \text{ ---- } 2\ Al_2O_3 + 12\ HCl$$

The fumed metal oxide particles have a smooth, substantially spherical surface and before being incorporated in the toner mass are preferably coated with a hydrophobic layer, e.g. formed by alkylation or by treatment with organic fluorine compounds. Their specific surface area is preferably in the range of 40 to 400 m^2/g.

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 0.1 to 10 % by weight.

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 may be present in the toner particle composition.

Instead of dispersing or dissolving (a) flow-improving additive(s) in the resin mass of the toner particle composition they may be mixed with the toner particles, i.e. are used in admixture with the bulk of toner particles. For that purpose zinc stearate has been 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. 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.

The toner powder particles according to the present invention are prepared by mixing the above defined binder and ingredients 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 sifting, cyclone separation or other classifying technique. The actually used toner particles have preferably an average diameter between 3 and 20 μm determined versus their average volume, more preferably between 5 and 10 μm when measured with a COULTER COUNTER (registered trade mark) Model TA II 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. The average diameter (size) of the toner particles derived from their average volume or weight is given by the instrument (see also ASTM Designation : F 577-83).

Suitable milling and air classification may be obtained when employing a combination apparatus such as the Alpine Fliessbeth-Gegenstrahlmühle (A.G.F.) 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.

To the obtained toner mass a flow improving agent is added in high speed stirrer, e.g. HENSCHEL FM4 of Thyssen Henschel, 3500 Kassel Germany.

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.

The present invention without limiting it thereto is illustrated by the following Example. All ratios, percentages and parts mentioned therein are by weight unless stated otherwise.

EXAMPLE 1 (comparative example)

Preparation of toner I (non-invention toner)

98 parts of resin No. 1 of Table 1 were melt-blended for 30 minutes at 110 °C in a laboratory kneader with 2 parts of Cu-phthalocyanine pigment (Colour Index PB 15:3).

After cooling the solidified mass was pulverized and milled using an ALPINE Fliessbettgegenstrahlmühle type 100AFG (tradename) and further classified using an ALPINE multiplex zig-zag classifier type 100MZR (tradename). The average particle diameter of the separated toner was measured by Coulter Counter model Multisizer (tradename) was found to be 8.3 μm by volume. In order to improve the flowability of the toner mass the toner particles were mixed with 0.5 % of hydrophobic colloidal silica particles (BET-value 130 m^2/g).

Preparation of toner II (non-invention toner)

The preparation of non-invention toner II proceeded as described for non-invention toner I with the difference that said resin No. 1 was replaced in equal amounts by resin No. 3 of Table 1.

Preparation of toner III (invention toner)

49 parts of resin No. 1 of Table 1 as resin P 1 and 49 parts of resin No. 3 of Table 1 as compound Q were melt-blended for 30 minutes at 110 °C in a laboratory kneader with 2 parts of Cu-phthalocyanine pigment (Colour Index PB 15:3).

After cooling the solidified mass was pulverized and milled using an ALPINE Fliessbettgegenstrahlmühle type 100AFG (tradename) and further classified using an ALPINE multiplex zig-zag classifier type 100MZR (tradename). The average particle size of the separated toner was measured by Coulter Counter model Multisizer (tradename) was found to be 8.0 μm by volume.

To improve the flowability of the toner mass the toner particles were mixed with 0.5 % of hydrophobic colloidal silica particles (BET-value 130 m^2/g).

The test R carried out on the mixture of said resins No. 1 and No. 3 resulted in a corrected absorption density value (A_{cor}) equal to 0.5.

Each of the above prepared toners I, II and III were used to form carrier-toner developers by mixing said mixture of toner particles and colloidal silica in a 4 % ratio with silicone-coated Cu-Zn ferrite carrier particles having an average diameter of 55 μm.

The thus obtained carrier toner-mixtures were used separately in an X-35 (tradename of Agfa-Gevaert N.V.) electrophotographic copier wherein the photoconductive drum was exposed to a step-wedge original.

From said X-35 copier the standard hot roller fuser was removed, and the toner of the unfixed copy was non-contact

fused by radiation using an infra-red black body radiant element placed at a distance of 10 mm from the copy paper carrying the toner image. The copy paper passed-by the radiant element at a speed of 5 cm per second. The average power provided to the radiant heating element was 375 W making the element operate at a temperature of 600 °C using reflectors to concentrate the radiant heat onto the copy paper.

On the fixed toner images gloss measurements were performed at a reflection angle of 60° according to DIN standard No. 67 530 (November 1972) between areas of the same low optical density (D_l = 0.25) and areas of substantially higher optical density (D_h - 1.60).

In the following Table 6 the obtained gloss measurement results are mentioned.

TABLE 6

Toner I		Toner II		Toner III	
D_l Gloss 14.3	D_h 30.6	D_l 7	D_h 14	D_l 10.0	D_h 10.5

From the measurement results in said Table 6 can be learned that with the invention-toner I almost equal gloss is obtained in the low and high density parts of the fixed toner image, whereas with the the comparative test toners I and II a substantial difference in gloss between said density values is obtained.

Claims

1. A dry toner powder of which the powder particles are electrostatically or magnetically attractable and suitable for use in the development of electrostatic charge images or magnetic patterns and wherein the composition of said powder particles includes at least one transparent thermoplastic resin P and at least one compound Q, said compound Q having a more polar character than said resin P, characterized in that said at least one resin P and said at least one compound Q when after been mixed in molten state followed by solidification form a light-scattering composition that under the measurement conditions of the test R as described herein has an optical absorption value of more than 0.10 but not more than 1.0, said resin(s) P and compound(s) Q being present in said toner in a weight ratio range P/Q from 5:1 to 1:5, and the weight ratio of P + Q with respect to the total weight of the toner is equal to or larger than 25:100.

2. Dry toner powder according to claim 1, wherein said weight ratio of P + Q with respect to the total weight of the toner is equal to or larger than 75:100.

3. Dry toner powder according to claim 1 or 2, wherein said weight ratio range P/Q is 3:1 to 1:3.

4. Dry toner powder according to any of claims 1 to 3, wherein said powder particles contain as resin P a first resin A being a polyester resin with low (less than 5.5 mol/kg) carbonyloxy group (-CO.O-) content, and a second resin B being a polyester with high (at least 7.5 mol/kg) carbonyloxy group content.

5. Dry toner powder according to claim 4, wherein said resin A is derived from a non-aromatic dicarboxylic acid and an ethoxylated and/or propoxylated Bisphenol A, and said resin B is a polyester derived from an aromatic dicarboxylic acid and a diol.

6. Dry toner powder according to claim 5, wherein in the production of said resin B the diol is ethylene glycol optionally mixed with ethoxylated and/or propoxylated Bisphenol A as long as the ethylene glycol content of the totality of diols is more than 50 mol %.

7. Dry toner powder according to claim 5, wherein said resin P is a polyester derived from fumaric acid and di-propoxylated Bisphenol A.

8. Dry toner powder according to any of claims 1 to 3, wherein said toner powder particles contain as resin P a polyester in combination with a compound Q being a styrene-acrylic resin having a relatively high (more than 70 mol %) styrene content.

9. Dry toner powder according to claim 1, wherein compound Q is at least one compound selected from the group consisting of arachidic acid and stearamide.

10. Dry toner powder according to any of the preceding claims, wherein said toner powder is colourless or contains a colorant.

Patentansprüche

1. Trockenes Tonerpulver, dessen Pulverteilchen elektrostatisch oder magnetisch anziehbar sind und das sich zur Verwendung bei der Entwicklung elektrostatischer Ladungsbilder oder magnetischer Muster eignet, wobei die Zusammensetzung der Pulverteilchen mindestens ein durchsichtiges thermoplastisches Harz P und mindestens eine Verbindung Q einschließt und die Verbindung Q einen polareren Charakter als Harz P aufweist, dadurch gekennzeichnet, daß das mindestens eine Harz P und die mindestens eine Verbindung Q nach dem Mischen in geschmolzenem Zustand und der Verfestigung eine lichtstreuende Masse bilden, die unter den Meßbedingungen des Tests R, wie hierin beschrieben, einen optischen Absorptionswert von mehr als 0,10, jedoch nicht mehr als 1,0 aufweist, wobei Harz(e) P und Verbindung(en) Q in dem Toner in einem Gewichtsverhältnis P/Q im Bereich von 5:1 bis 1:5 vorliegen und das Gewichtsverhältnis von P + Q hinsichtlich des Gesamtgewichtes des Toners gleich oder größer als 25:100 ist.

2. Trockenes Tonerpulver nach Anspruch 1, wobei das Gewichtsverhältnis von P + Q hinsichtlich des Gesamtgewichtes des Toners gleich oder größer als 75:100 ist.

3. Trockenes Tonerpulver nach Anspruch 1 oder 2, wobei der Bereich des Gewichtsverhältnisses P/Q 3:1 bis 1:3 ist.

4. Trockenes Tonerpulver nach einem der Ansprüche 1 bis 3, wobei die Pulverteilchen als Harz P ein erstes Harz A, das ein Polyesterharz mit einem geringen (weniger als 5,5 Mol/kg) Carbonyloxy(-CO.O-)gruppenanteil ist, und ein zweites Harz B, das ein Polyester mit hohem (mindestens 7,5 Mol/kg) Carbonyloxygruppenanteil ist, enthalten.

5. Trockenes Tonerpulver nach Anspruch 4, wobei das Harz A von einer nichtaromatischen Dicarbonsäure und einem ethoxylierten und/oder propoxylierten Bisphenol A abgeleitet ist und das Harz B ein Polyester aus einer aromatischen Dicarbonsäure und einem Diol ist.

6. Trockenes Tonerpulver nach Anspruch 5, wobei bei der Herstellung des Harzes B das Diol Ethylenglycol ist, gegebenenfalls vermischt mit ethoxyliertem und/oder propoxyliertem Bisphenol A, solange der Ethylenglycolanteil der Diolgesamtmenge mehr als 50 Mol-% beträgt.

7. Trockenes Tonerpulver nach Anspruch 5, wobei das Harz P ein Polyester aus Fumarsäure und einem dipropoxylierten Bisphenol A ist.

8. Trockenes Tonerpulver nach einem der Ansprüche 1 bis 3, wobei die Tonerpulverteilchen als Harz P einen Polyester in Kombination mit einer Verbindung Q enthalten, bei der es sich um ein Styrol-Acrylharz mit einem relativ hohen (mehr als 70 Mol-%) Styrolgehalt handelt.

9. Trockenes Tonerpulver nach Anspruch 1, wobei es sich bei der Verbindung Q um mindestens eine unter Arachinsäure und Stearamid ausgewählte Verbindung handelt.

10. Trockenes Tonerpulver nach einem der vorangehenden Ansprüche, wobei das Tonerpulver farblos ist oder ein Färbemittel enthält.

Revendications

1. Poudre de toner sec dont les particules de poudre sont sujettes à une attraction électrostatique ou magnétique et conviennent pour une utilisation dans le développement d'images de charge électrostatique ou de dessins magnétiques, et dans lesquelles lesdites particules de poudre renferment au moins une résine thermoplastique P transparente et au moins un composé Q, ledit composé Q ayant un caractère plus polaire que ladite résine P, caractérisé en ce que ladite résine P, au nombre d'au moins un, et ledit composé Q, au nombre d'au moins un, après avoir été mélangés dans l'état fondu, puis solidifiés, forment une composition diffusant la lumière qui, dans les conditions de mesure de l'essai R décrit dans la description, possède une valeur d'absorption optique corrigée supérieure à 0,10, mais pas supérieure à 1,0, ladite ou lesdites résines P et ledit ou lesdits composés Q étant présents, dans ledit

toner, dans un rapport pondéral P/Q de 5:1 à 1:5, et le rapport pondéral de P + Q, rapporté au poids total du toner, est égal ou supérieur à 25:100.

2. Poudre de toner sec selon la revendication 1, dans laquelle ledit rapport pondéral de P + Q rapporté au poids total du toner est égal ou supérieur à 75:100.

3. Poudre de toner sec selon la revendication 1 ou 2, dans laquelle ledit rapport pondéral P/Q est de 3:1 à 1:3.

4. Poudre de toner sec selon l'une quelconque des revendications 1 à 3, dans laquelle lesdites particules de poudre contiennent, comme résine P, une première résine A qui est une résine de polyester possédant une faible teneur (inférieure à 5,5 moles/kg) en groupes carbonyloxy (-CO.O-), et une seconde résine B qui est un polyester possédant une forte teneur (supérieure à 7,5 moles/kg) en groupes carbonyloxy.

5. Poudre de toner sec selon la revendication 4, dans laquelle ladite résine A est dérivée d'un acide dicarboxylique non aromatique et d'un bisphénol A éthoxylé et/ou propoxylé, et ladite résine B est un polyester dérivé d'un acide dicarboxylique aromatique et d'un diol.

6. Poudre de toner sec selon la revendication 5, dans laquelle, dans la production de ladite résine B, le diol est l'éthylèneglycol, éventuellement mélangé avec du bisphénol A éthoxylé et/ou propoxylé, pourvu que la teneur en éthylèneglycol de la totalité des diols soit supérieure à 50% en moles.

7. Poudre de toner sec selon la revendication 5, dans laquelle ladite résine P est un polyester dérivé de l'acide fumarique et du bisphénol A dipropoxylé.

8. Poudre de toner sec selon l'une quelconque des revendications 1 à 3, dans laquelle lesdites particules de poudre de toner contiennent, comme résine P, un polyester en combinaison avec un composé Q qui est une résine styrène-acrylique ayant une teneur en styrène relativement élevée (supérieure à 70% en moles).

9. Poudre de toner sec selon la revendication 1, dans laquelle le composé Q est au moins un composé choisi parmi l'acide arachidique et le stéaramide.

10. Poudre de toner sec selon l'une quelconque des revendications précédentes, dans laquelle ladite poudre de toner est incolore ou contient un colorant.