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DRY ELECTROSTATOGRAPHIC TONER COMPOSITION.

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DE-A- 3 516 937
FR-A- 2 569 874
GB-A- 2 180 948
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Description

The present invention relates to a toner composition consisting of fusible electrostatically attractable toner particles suitable for development of electrostatic charge patterns.

It is well known in the art of electrographic and electrophotographic copying and printing to form an electrostatic latent image corresponding to either the original to be copied, or corresponding to the digitized data describing an electronically available image, on a photoconductive member. In another image forming method, the electrostatic latent image is formed by imagewise discharge over styli towards a dielectric substrate. The xeroprinting process such as disclosed e.g. in European Patent Application 0 243 934 involves imagewise exposing a photopolymer master, charging on a conductive support, toning with dry or liquid toner and transferring to another substrate.

Electrostatic latent images can be developed using a liquid developer consisting of a colloidal system of charged colloidal particles in an insulating liquid. 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 support sheet bearing the toner powder image is subsequently passed through a fusing apparatus and is thereafter discharged out of the copying resp. printing machine as a final copy, resp. final print.

As is apparent from the above brief description of the overall electrostatographic process two essential stages should be considered. First a latent electrostatographic image is formed on a suitable member, e.g. a photoconductive drum, secondly this latent image is developed to form a visually discernible image and transferred in a transfer station to a final hard copy.

One of the objectives set forth for the overall electrostatographic process is to provide an image on the final copy, resp. final print with the best possible quality.

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

Quality consequently comprises features such as uniform darkness of the image areas, background quality, clear delineation of lines, as well as overall resolution of the image.

In an optical electronic printing apparatus, the 'quality' and more in particular the resolution of the latent electrostatographic image is determined by the accuracy of each of the following steps : first the conversion of the digitized data describing the electronically available image to an appropriate illumination pattern, secondly the illumination of the photoconductive drum by the laser or light emitting diode system; thirdly the resolving power of the photoconductive process present on the photoconductive drum. In the case of a xeroprinting device the quality of the latent electrostatic image is determined by the contact exposure step.

In a copying apparatus the 'quality' of the latent electrostatographic image is predominantly determined by the accuracy of illumination of the photoconductive drum by the electro-optical system, whereby the optical quality of the mirrors, lenses, optical fibres, etc. used, as well as the solidity, sturdiness and lack of vibrations of the construction play a vital role.

As is set forth in 'Electrophotography' written by R.M.Schaffert and published by the Local Press Ltd., London, Enlarged and Revised Edition, 1975, page 93, item 2.15.8 "Resolution", the resolution of a latent electrostatic image on a xerographic plate such as one of amorphous selenium, is inherently very high since the photoconductive film is essentially grainless. The same holds for molecular Organic Photo-Conducting materials.

Further it is noted in general that the first stage of the overall electrostatographic process, i.e. the illumination of the photoconductive drum, is in most cases, where the necessary care has been taken in respect of overall construction of the device, not a limiting factor in respect of the overall attainable resolution of the xerographic print.

As neither the illumination for the photoconductive drum, nor the photoconductive drum itself limit the resolution of the final print or copy resulting from the overall electrostatographic process, the critical factor in respect of the overall image quality is the second stage of the electrophotographic process, i.e. the conversion of the latent image into a visually discernible image.

The overall accuracy by which the latent electrostatographic image, formed in either an electronic printing or copying apparatus, is developed into a visually discernible copy is predominantly determined by the characteristics of the developer used.

It is known that one of the principal contributing characteristics hereof 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' the influence of toner particle diameter and shape upon image quality, particularly for high resolution images, has been tested.

For a developer to be used in a high resolution laser beam printer, the effects of toner particle size and

shape upon the image were experimentally examined. As a result it was made clear that apart from the shape of the toner and its charge distribution, fine particles are most effective to provide high resolution.

This fact being known in itself, there have been several prior art proposals for the manufacture of fine toner particles and in particular for toner particles, the size distribution of which meets a well-defined classification.

In U.S. Patent 3,942,979 assigned to Xerox Corp. toner materials are claimed with a particle size distribution wherein less than about 30 % percent by number of the toner particles have an average particle size diameter of less than about 5 microns, about 25 % by number of the particles have a diameter between about 8 microns and about 12 microns, and less than about 5 % by number of the toner particles have an average particle diameter greater than about 20 microns.

According to a preferred embodiment of the invention claimed in the cited patent, less than about 10 % by number of the toner particles have an average particle diameter of less than about 5 microns, about 60 % by number of the toner particles have an average particle diameter of between about 8 and about 12 microns, and less than about 5 % by number of the toner particles have an average particle diameter greater than about 20 microns.

In U.S. Patent 4,284,701 assigned to IBM Corp., toner particles are claimed according to a size distribution wherein less than 15% by weight are greater than 16 microns, between 7 and 15 % by weight are less than 5 microns, the remainder being from 5 to 16 microns and wherein the median particle size by weight is from 8 to 12 microns.

As it is generally known that the resolution of an electrostatographic print is determined, apart from the size distribution of the toner particles, by the average or median size of the toner particles, efforts have been made to manufacture and use extremely fine developer materials.

However the smaller the average size of the toner particles, or the greater the fraction of the very small toner particles in the overall toner size distribution, the greater the tendency of the toner and of the overall developer composition to agglomerate, or to cluster together. So the limited flow characteristics of dry electrostatic toner are a limiting factor in respect of the use of very fine toner particles. Consequently when high resolution is set forth as a prerequisite in a particular electrophotographic process, liquid developer compositions are often used.

Indeed, liquid developer compositions with toner particles having average or median particle sizes as fine as 0.25 microns are known for producing very high resolution electrostatic prints. For those skilled in the art, flocculation can be prevented by optimizing the colloidal forces. Liquid developer compositions suitable for use in developing electrostatic charge patterns are disclosed e.g. in U.S. Patents 4,123,374 and 4,138,351 both assigned to Agfa-Gevaert N.V., Mortsel, Belgium.

Liquid developers however exhibit an important drawback : the dielectric solvent carried along with the toner and simultaneously deposited to the electrostatographic print should be evaporated and consequently recycled or disposed of in the atmosphere so as to obtain a dry final print.

In comparison to the dry electrophotographic process, an electrostatographic apparatus employing a liquid developer consequently entails much inconvenience for the customer.

Therefore in spite of the limited flow characteristics of very fine dry electrostatographic toner particles, efforts have been made for the manufacture of such fine toners.

U.K. Patent Application GB 2,180,94B discloses the use of toner particles of size not more than 5 microns. By the use of such small toner particles the resolution of the image has been 10 lines/mm while it is 5 lines/mm when the particle size of the toner is approximately 10 microns. In order to avoid sticking of the toner particles to the image bearing member, a lubricant, e.g. zinc stearate, should be added in an amount of at least 0.5 wt%.

European Patent 0 255 716 discloses a process for the manufacture of fine toner particles having a uniform spherical particle form. According to said application the volume average particle size by a Coulter Counter method is from 1.0 to 7.0 micron and the number average particle size is from 1.0 to 5.0 micron.

In order to have improved fluidity and charging property, said toner particles are manufactured according to a complex suspension polymerization process. United States Patent 4,737,433 discloses an electrostatographic process wherein toner particles having an average diameter less than 10 micron are used. In this application it is said that fundamental difficulties arise when trying to transfer toner particles having an average diameter less than 10 micron from the image bearing member to the paper support in the electrostatographic transfer station, and suitable remedies are proposed.

In Japanese Patent Application 85 JP-192711, the formation of sharp images having excellent resolving power by an electrostatographic process is described whereby toner particles with grain size between 1-5 micron are employed. The development of the latent image on the photoconductive drum is executed without contact between the photoconductive drum and the thin developer layer applying means.

It is therefore an object of the present invention to provide dry developer materials that exhibit superior performance over the prior art dry developer materials in terms of overall quality of the final electrostatographic

print, and in terms of overall performance in the electrostatographic process.

We have now found that the above objects are accomplished by providing electrostatographic toner particles comprising classified toner particles having a particle size distribution wherein

- more than 90 percent by volume of the toner particles have equivalent particle size diameters larger than 0.5 micrometer, and less than 7 micrometer, and,
- more than about 50 percent by volume of the toner particles have equivalent particle size diameters of less than about 5 micrometer,

whereby said toner particles have on their surface fine inorganic microparticles acting as flow enhancing additives in a concentration of at least 0,1% w/w and at most 5% w/w, said fine inorganic microparticles being characterized by a product of specific surface area $A(m^2/g)$ times methanol value $B(\% V/V)$ fulfilling the relation:

$$A \times B > 10.000$$

and whereby the ratio of the apparent density over the bulk density of the toner particles satisfies the following equation :

$$\frac{\rho_{app}}{\rho_{bulk}} > 0.2$$

According to a preferred embodiment of the present invention, more than 90 % by volume of the toner particles have equivalent particle size diameters larger than 0.5 micron and less than 6 micron, and more than about 50 percent by volume of the toner particles have equivalent particle size diameters of less than about 4 microns.

According to a further preferred embodiment, more than 90 % by volume of the toner particles have equivalent particle size diameters larger than 0.5 micron and less than 5 micron, and more than about 50 percent by volume of the toner particles have equivalent particle size diameters of less than about 3 microns.

According to a further preferred embodiment, the toner particles are admixed with fine inorganic microparticles, which are coated with hydrophobic groups containing entities, resulting in a methanol value larger than 20.

Furtheron, a preferred embodiment comprises toner with admixed fine inorganic microparticles, having a specific surface no larger than $150 m^2/g$.

The toner compositions suitable for use in accordance with the present invention should be prepared by selecting and modifying some of the known toner mixing and comminution techniques. As is generally known toner is prepared by subsequently blending and mixing the components in the molten state and after cooling, milling and micropulverizing the resulting mixture. Thereafter so as to obtain toner particles corresponding to predetermined particle-sizes, a suitable particle classification method is employed. Typical particle classification methods include air classification, screening, cyclone separation, elutriation, centrifugation and combinations thereof.

The preferred method of obtaining the very fine toner particles of our invention is by centrifugal air classification.

Suitable milling and air classification results may be obtained when employing a combination apparatus such as the A.F.G. (Alpine Fließbeth-Gegenstrahlmühle) type 100 as milling means, equipped with an A.T.P. (Alpine Turboplex windsichter) type 50 G.S., as air classification means, the model being available from Alpine Process Technology Ltd., Rivington Road, Whitehouse, Industrial Estate, Runcorn, Cheshire, U.K. Further air classification can be realised using an A 100 MZR (Alpine Multiplex Labor Zick-zack sichter) as additional classification apparatus, the latter model being also available from Alpine Process Technology Ltd. The size distribution of the so obtained toner particles can be determined in a conventional manner by employing a Coulter Counter type TA II/PCA1, model available from the Coulter Electronics Corp., Northwell Drive, Luton, Bedfordshire, LV 33 R4, United Kingdom.

In the air classification apparatus, air or some other gas is used as transport medium and particles contained in the fluidum are exposed to two antagonistic forces, viz., to the inwardly directed tractive force of the fluidum, and to the outwardly directed centrifugal force of the particle. For a definite size of particles, that is, the "cut size", both forces are in equilibrium. Larger (heavier) particles are dominated by the mass-dependent centrifugal force and the smaller (lighter) particles by the frictional force proportional to the particle diameter. Consequently, the larger or heavier particles fly outwards as coarse fraction, while the smaller or lighter ones are carried inwards by the air as fine fraction. The "cut size" usually depends upon the geometrical as well as operational parameters (dimensions of classification, rotor, rotational velocity, etc.). Adjustment of the cut size may be effected through variation of the above mentioned parameters.

Although by application of the mentioned preparation methods toner particles may be prepared which are in accordance with the aforementioned size distribution as claimed, these toner particles as such exhibit problems when used in electrostatographic copying or printing apparatus as their flowability and hence forth overall

performance in the electrostatographic process is insufficient.

We have found that by adding suitable flow improving agents in a selected way, the flowability of the so prepared toner particles can be sufficiently enhanced so as to obtain toner particles suitable for use in electrostatographic apparatus.

In order to improve the flow properties of toner the toner particles may be admixed with flow enhancing additives. These additives mostly are extremely fine inorganic materials. Widely used in this context are fumed inorganics such as silica, alumina or zirconium oxide or titanium oxide. The use of silica as flow improving agent for toner compositions is described in the United Kingdom Patent Specification No. 1,438,110.

The fumed silica particles used in the toner composition of the present invention are essentially spherical, and have a surface coated with hydrophobic layer such as obtained by reaction between silanol groups of the silica-type micro-particles and silanes of different types and volumes, whereby reference is made to EP 0234009 (of Toray Silicone Co.). Other microparticles may also be used showing comparable properties and preparation-procedures.

The nature of the surface can be changed, also the coverage degree. Where chemically reacted coating groups are preferred, physically absorbed coatings also fulfill the conditions of the present invention, showing on long term developing processes with the potential drawback of filming on the image bearing member and other machineparts.

Fumed silica particles with surface area larger than 150m²/g and methanol values larger than 20 are commercially available under the Trade Marks Aerosil and CAB-O-SIL marketed by Degussa, Frankfurt (M), W.Germany and Cabot Corp. Oxides Division, Boston, Mass., U.S.A. respectively. AEROSIL R972 is a typical example of fumed hydrophobic silica having a specific surface area of 110 sq.m/g and a methanol value of 40.

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. 8 (1958) 1387-1390.

The methanol value can be determined by the following procedure. 200mg of the powder and 50 ml water are put in a vibration flask of 250 ml and stirred magnetically. Methanol is added at a rate not exceeding 10 ml/ 5 minutes. The end point of titration is determined as the point where all powder is suspended (x ml). The methanol value (B) is then calculated as :

$$B = \frac{X \times 100}{50 + X}$$

Commercially available types and specially prepared samples were used in the present invention.

The preferred proportions of fumed silica to toner material are in the range of 0.5 to 3 % by weight.

The toner compositions used in accordance with the present invention may comprise conventional resin binders such as those disclosed e.g. in European Patents 0 128 569 and 0 170 421, and European application no.89200192.6. Interesting examples are disclosed in European patent 0 279 960, being copolymers of

(1) styrene or styrene homologue,

(2) an alkyl acrylate or alkyl methacrylate monomer of which the alkyl chain comprises at least 8 carbon atoms in straight line, and

(3) a crosslinking monomer containing at least two ethylenically unsaturated groups,

Partly crosslinked polyesters are also interesting types, e.g. those disclosed in published GB-A-2082788A, being e.g. binder-compositions derived from terephthalic acid that is polycondensed with less than 1 equivalent of an ethoxylated and/or propoxylated "bisphenol A". Further any of the other usual polymeric resins suitable for use as binder in toner particles can be used.

For further optimizing the toner properties other resins or pigments modifying the melt viscosity and/or release agents may be used. In particular when the heated roller fusing process is employed, additional release agent, assisting in the release of the toner melt from the fuser roller, should advantageously be incorporated in the toner composition. Particularly suited release agents are adhesion promoting compounds, e.g. talcum, silicones, fluor containing polymers and natural or synthetic waxes.

Suitable fluor-containing vinyl polymers having a particularly low friction coefficient (static friction coefficient with respect to steel below 0.2) for preventing toner offsetting on the fuser roll are described in US-A-4,059,768.

Particularly suitable for preventing toner-offsetting are waxy polyalkylene resins, more particularly an isotactic polypropylene having an average molecular weight lower than 15,000.

The coloring substance used in the toner particles may be any inorganic pigment (including carbon) or solid organic pigments or dyes, or mixtures thereof commonly employed in dry electrostatic toner compositions. Thus, use can be made e.g. of carbon black and analogous forms thereof, such as lamp black, channel black, and furnace black e.g. SPEZIALSCHWARZ IV (trade-name of Degussa Frankfurt/M, W.Germany) and CABOT REGAL 400 (trade name of Cabot Corp. High Street 125, Boston, U.S.A.).

The addition of colorants may also influence the melt viscosity of the toner and if desired, the addition of colorants may be considered that bring the melt viscosity of the toner in the desired range. The colorants can be added and mixed with the molten toner composition that on cooling is crushed and ground to obtain the desired particle size.

5 Apart from the above-mentioned coloring agents the use of viscosity regulating pigments can be considered. Interesting types for that purpose are titanium dioxide (rutile), barium sulphate (barite), calcium carbonate (calcite), ferric oxide (Fe_2O_3 = hematite) and ferrosferric oxide (Fe_3O_4 = magnetite), cupric oxide; other magnetic or magnetizable pigments can also be used.

10 The latter pigments can serve also as coloring substance e.g. in magnetic toners. Therefore, the present invention includes toners wherein one or more coloring substances are present.

The typical solid organic dyestuffs used in electrophotographic toners are the so-called pigment dyes, which include phthalocyanine dyes, e.g. copper phthalocyanines, metal-free phthalocyanines, azo dyes, and metal complexes of azo dyes.

15 The following dyes in pigment form are given for illustration purposes only : FANALROSA B Supra Pulver (trade name of BASF AG, Ludwigshafen, Western Germany), HELIOGENBLAU LG (trade name of BASF for a metal-free phthalocyanine blue pigment), MONASTRAL BLUE (a copper phthalocyanine pigment, C.I. 74,160), HELIOGENBLAU B Pulver (trade name of BASF), HELIOECHTBLAU HG (trade name of Bayer AG, Leverkusen, Western Germany, for a copper phthalocyanine C.I. 74,160), BRILLIANT CARMINE 6B (C.I. 18,850), and VIOLET FANAL R (trade name of BASF, C.I. 42,535).

20 The typical inorganic pigments used in electrophotography include carbon black, black iron (III) oxide and mixed copper(II) oxide/chromium(III) oxide/iron(III)oxide powder, milori blue, ultramarine cobalt blue, and barium permanganate. Further can be mentioned : the pigments described in the French Patent Specifications 1,394,061 filed December 23, 1963 by Kodak Ltd. and 1,439,323 filed April 27, 1965 by Harris Intertype Corporation.

25 The coloring substance is normally used in a concentration range from 5 to 20 % by weight, calculated with respect to the total weight of the toner.

Apart from insoluble coloring substances the use of soluble coloring substances can also be considered.

To enhance the chargeability in either negative or positive direction of the toner particles (a) charge control agent(s) is (are) added to the toner particle composition as described e.g. in the published German patent application (DE-OS) 3,022,333 for yielding negatively chargeable toner particles or as described e.g. in the published German Patent application (DE-OS) 2,362,410 and the United States Patent Specifications 4,263,389 and 4,264,702 for yielding positively chargeable toner particles. A very useful charge control agent for offering positive charge polarity is BONTRON N04 (trade name of Oriental Chemical Industries - Japan) being a resin acid modified nigrosine dye which may be used e.g. in an amount up to 5 % by weight with respect to the toner particle composition. A very useful charge control agent for offering negative charge polarity is BONTRON S36 (trade name of Oriental Chemical Industries - Japan) being a metal complex dye which may be used e.g. in an amount up to 5 % by weight with respect to the toner particle composition.

35 In the preparation of the toner the coloring material and other additives are added to the molten resin and are subjected to kneading until a homogeneous mixture is obtained. After cooling, the solid mass obtained is crushed and ground e.g. in a hammer mill followed by a jet-mill. After this operation, air classification was effected.

40 For a given charge density of the latent image charge-carrying surface the maximum development density attainable with toner particles of a given size is determined by the charge/toner particle mass ratio, which is determined substantially by the triboelectric charge obtained by friction contact with carrier particles in case of a two-component developer.

45 The toner compositions of the present invention preferably should be used in combination with carrier particles.

The development may proceed by so-called cascading the toner particles over the imaging surface containing the electrostatic charge pattern or with magnetic brush. The carrier particles may be electrically conductive, insulating, magnetic or non-magnetic (for magnetic brush development they must be magnetic), as long as the carrier particles are capable of triboelectrically obtaining a charge of opposite polarity to that of the toner particles so that the toner particles adhere to and surround the carrier particles.

50 In developing an electrostatic image to form a positive reproduction of an original, the carrier particle composition and/or toner particle composition is selected so that the toner particles acquire a charge having a polarity opposite to that of the electrostatic latent image so that toner deposition occurs in image areas. Alternatively, in reversal reproduction of an electrostatic latent image, the carrier particle composition and toner particle composition is selected so that the toner particles acquire a charge having the same polarity as that of the electrostatic latent image resulting in toner deposition in the non-image areas.

Useful carrier materials for cascade development include sodium chloride, ammonium chloride, aluminium potassium chloride, Rochelle salt, sodium nitrate, aluminium nitrate, potassium chlorate, granular zircon, granular silicon, silica, methyl methacrylate, glass. Useful carrier materials for magnetic brush development include, steel, nickel, iron, ferrites, ferromagnetic materials, e.g. magnetite, whether or not coated with a polymer skin. Other suitable carrier particles include magnetic or magnetizable materials dispersed in powder form in a binder as described e.g. in US-A-4,600,675. Many of the foregoing and typical carriers are disclosed in U.S. Patents 2,618,441; 2,638,416; 2,618,522; 3,591,503 and 3,533,835 directed to electrically conductive carrier coatings, and US-A-3,526,533 directed to polymer coated carriers. Oxide coated iron powder carrier particles are described e.g. in U.S. Patent 3,767,477. The U.S. Patents 3,847,604 and 3,767,578 relate to carrier beads on the basis of nickel. An ultimate coated carrier particle diameter between about 30 microns to about 1000 microns is preferred. The carrier particles possess then sufficient inertia to avoid adherence to the electrostatic images during the cascade development process and withstand loss by centrifugal forces operating in magnetic brush development. The carrier may be employed with the toner composition in any suitable combination, generally satisfactory results have been obtained when about 1 part of toner is used with about 5 to about 200 parts by weight of carrier.

The toner compositions of the present invention may be used to develop electrostatic latent images on any suitable electrostatic surface capable of retaining charge, particularly photoconductive layers known in the art including conventional photoconductors. Hot roll fusing of toners is described e.g. in Journal of Imaging Technology, Vol. 11, No. 6, Dec. 1985, p. 261-279 and the heated roller fusing process as well as an electrostatographic apparatus for implementing this process is set forth in detail in the already cited European patent 0 279 960, whereas infra-red fusing is described in U.S. Patent 4,525,455.

The following examples illustrate the invention without, however, limiting it thereto. All parts, ratios and percentages are by weight.

Examples : detailed procedure

Toner preparation

90 parts of ATLAC T500 (trade name of Atlas Chemical Industries Inc., Wilmington, Del., USA) being a propoxylated bisphenol A fumarate polyester with a glass transition temperature of 51°C, a melting point in the range of 65° to 85°C, an acid number of 13.9, and an intrinsic viscosity measured at 25°C in a mixture of phenol/ortho dichlorobenzene (60/40 by weight) of 0.175, 10 parts of Cabot Regal 400 (trade name of Cabot Corp., Boston, Mass., USA) being a carbon black, were introduced in a kneader and heated at 120°C to form a melt, upon which the kneading process was started. After about 30 minutes, the kneading was stopped and the mixture was allowed to cool to room temperature (20°C). At that temperature the mixture was crushed and milled to form a powder, which was further reduced in grain size by jet milling. Further, air classification using the above mentioned apparatus was effected.

The size distribution of the toner was then determined in a Coulter Multisizer apparatus with a measuring tube of 30 micron, the results of which are set forth hereunder in Table no. 1.

Table 1

	Diam.	Vol. % Dif.	Vol. % Cum.
5	1.00	9.51	100.02
	1.26	21.93	90.51
	1.59	40.94	68.58
10	2.00	22.98	27.64
	2.62	3.27	4.66
	3.18	.26	1.39
	4.01	.12	1.13
15	5.05	.08	1.01
	6.36	.00	.93
	10.09	.31	.93
20	12.71	.62	.62
	16.01	.00	.00

Column 2 of this table lists the differential percentages of toner particles by volume situated between the equivalent spherical diameter (in microns) set forth in column 1.

Column 3 of this table sets forth the percentage values of column 2 on a cumulative basis.

Analysis of the size distribution of toner particles prepared according to the above described procedure shows the following results : percentage of particles by volume larger than 3 micron : about 2.5 % percentage of particles by volume larger than 4 micron : about 1 % percentage of particles by volume larger than 5 micron : about 1 %.

Hereupon, the selected toner particles were introduced in a mixing apparatus and Aerosil R812 (a trade name of Degussa AG, Germany), being a fumed hydrophobic silica with a specific surface of 260 m²/g and methanol value 56 and an average particle diameter of 7 nm, was admixed to the toner as follows.

To 100 g of toner particles, 0.5 g of fumed silica particles were added in a metal box (with a diameter of 10 cm) containing 100 ceramic balls with average diameter of 9 mm, and density of 2.4 g/cm³. This mixture was then rotated at a speed of 300 rpm, for a period of 30 minutes (this method is referred to in table 2 as method A).

An alternative method which can be used is adding the toner and the flow enhancing additive to a Janke and Kunkel labor-mill apparatus type IKAM20, rotating at a speed of 20.000 rpm, and thermostabilised at 20°C. This model is available from the Janke and Kunkel GmbH, IKA Labortechnik, D-7813 Staufen, W. Germany. This method of admixing the flow enhancing additives to the toner is referred to as method B in Table 2.

Development and transfer

An electrostatic image formed on an electrophotographic recording element (i.e. an As₂Se₃ coated conductive drum, which was positively charged and image-wise exposed to light), was developed by a magnetic brush which was built up with a developer obtained by mixing the obtained toner with a typical carrier such a ferrite carrier (Ni-Zn type), with a magnetisation of 50 EMU/g. The average carrier particle diameter was on or about 65 micron.

After addition of the toner particles to the carrier in an amount of 2,5 % by weight with respect to the carrier, the developer is activated by rolling in a metal box with a diameter of 6 cm, at 300 revolutions per minute, during a period of 30 minutes, with an apparant degree of filling of 30 %.

In case the average equivalent toner particle diameter is larger, the amount of toner as percent to the weight of the carrier, should be larger; this implies that in both cases the amount in terms of surface coverage of toner to the carrier remains equal.

The transfer of the electrostatically deposited toner proceeded by applying a positive voltage of 3 kV to a metal roll, which was kept in close ohmic contact with the rear side of a paper sheet acting as receiving material whose front side was therefore kept in close contact with the toner image on the photoconductor.

Fusing

The image-wise transferred toner particles were fed to a radiation fusing device operating with an infra-red light fusing element such as described in the text of Example 8 of US Patent 4,525,445.

Evaluation of copy quality

When toner particles with a conventional size distribution, e.g. characterised by an average particle size diameter of 10 to 15 microns are used, the resolution of the overall electrostatographic process in a conventional copier is limited to lines of about 35 microns; this means that a line pair structure whereby the distance between successive black lines is less than 35 microns cannot be faithfully reproduced by the overall electrostatographic process. However, with the toner according to the present invention lines with a thickness down to 25 microns were faithfully reproduced from the original on to the final copy.

The above was determined as follows : a wedge according to UGRA - Offset-Testkeil 1982 compatible with the FOGRA-PMS-System, edited by the 'Deutsche Forschungsgesellschaft für Druck und Reproduktionstechnik e.V., Postfach 80 04 69, Streitfeldstrasse 19, D-8000 München, was copied in an electrostatographic apparatus as described above.

Said wedge exhibits figures consisting of concentric circles with increasing resolution. The ultimate resolution on the final copy - corresponding with the finest concentric circles visually discernible on said copy, made in an electrostatographic process as described above, was 25 microns.

When the conventional optical system for illuminating the photoconductive drum was replaced by a high-quality optical device the ultimate resolution on the final copy was 8 microns, when using the toner according to the present invention.

Determination of bulk and apparent density and density ratio

The bulk density of the toner particles is measured in accordance with conventional techniques in an apparatus such as the Beckmann Air Comparimeter, model available from Beckmann Instruments, Chemin des Bourdon nr. 52-54, 93220 Gagny, France.

The apparent density of the toner particles is determined according to the following procedure.

100 g of toner particles are shaken for a few minutes in a bottle with a volume of approximately 500 ml and are thereafter put on a vibrating sieve with a diameter of 7 cm, a mesh size of 1 mm, vibrating at a frequency of 50 Hz and an amplitude of 1 mm. The agitated toner particles are fed through the sieve to a flat cylindrical recipient with a height of 1.7 cm and a diameter of 7 cm. After equilibration for 2 minutes the toner particles exceeding the height of the recipient are scraped off and the weight of the toner particles contained in the recipient is determined. The apparent density is then calculated as follows :

$$\rho_{\text{app}} = \frac{\text{weight of the toner particles as measured}}{\text{volume of the recipient}}$$

Examples : evaluation

In the Table 2 hereunder are set forth the experimental results of toners, made according to the above described procedure, whereby the milling and classification parameters were varied, as well as the concentration and method of addition of the flow enhancing additive. The resolution on the final copy in an electrostatographic process using these toners is also set forth.

The results in terms of average diameter of the toner particles, of the ratio of bulk over apparent density and of the ultimate resolution, are set forth hereunder in Table 2. The bulk density of the toner particles was 1.17 kg/dm³.

The particle size distribution of the toners of ref. numbers 1, 2 and 3 fulfill the cited criterium. The same holds for the packing criterium. The observed resolution is very good. Deviation from particle size criterium rapidly induces decrease in image quality, even if the packing criterium is fulfilled.

Table 2

Ref.no.	d	d _v	d _n	ρ_{app}/ρ_{bulk}	resol 1	resol 2
1	2.6	2.8	2.4	0.21	25	8
2	3.6	4.1	3.2	0.26	25	10
3	4.5	5.0	4.0	0.25	20	12
4	5.7	6.3	5.0	0.31	25	12
5	6.7	7.5	6.0	0.32	25	19
6	11.3	13.5	9.5	0.31	40	30

In the above Table 2,

d_v represents the average diameter of the toner particles by volume,

d_n represents the average diameter of the toner particles by number,

d represents $(d_v \times d_n)^{1/2}$,

resol 1 represents the thickness in microns of the finest lines on the original test wedge which still were faithfully reproduced on the final copy made in an electrostatographic apparatus as described above in the example, being a conventional copier;

resol 2 represents the thickness in microns of the finest lines on the original test wedge which still were faithfully reproduced on the final copy made in an electrostatographic apparatus as described above, but whereby the conventional optical system for illuminating the photoconductive drum is replaced by a high-quality optical device;

ρ_{app}/ρ_{bulk} represents the ratio of the apparent density over the bulk density of the toner particles.

From the above results it is also apparent that, provided the illumination of the photoconductive drum is executed by a high-quality optical system the resolution attainable with the toner according to the present invention is up to 8 microns.

The particle size distribution of the toner with reference number 2 in the above Table 2 is set forth hereinafter. This toner was prepared according to the same procedure as set forth above but a different size distribution was obtained due to different milling and classification settings of the A.F.G./A.T.P. Alpine combination apparatus described above.

Table 3

	Diam.	Vol % Dif.	Vol % Cum.
5	1.59	1.13	100.01
10	2.00	3.44	98.88
	2.52	10.34	95.44
	3.19	26.97	85.10
	4.01	44.79	58.13
15	5.05	11.52	13.34
	6.36	.39	1.82
	8.01	.29	1.43
20	10.09	.19	1.14
	12.71	.19	.95
	16.01	.00	.76
25	20.17	.76	.76
	25.41	.00	.00

The columns two and three have the same meaning as the corresponding columns of Table 1. Analysis of the size distribution shows the following results :

percentage of particles by volume larger than 3 micron : 88 %
percentage of particles by volume larger than 4 micron : 58 %
percentage of particles by volume larger than 5 micron : 15 %

However, apart from the high attainable resolution of the toner particles according to the present invention, various process characteristics of the electrostatographic process also have to be taken into account when evaluating the overall technical performance of the particular developer composition.

Therefore the electrostatographic process characteristics of toner compositions prepared according to the above-described procedure were evaluated.

Table 4

	Ref. number	d_v	d_n	d	conc.	ρ_{app}/ρ_{bulk}	method	toner weight	time
45	7	7.79	5.31	6.4	0.3	0.43	B	50	5
	8	4.16	2.76	3.4	3	0.32	B	75	80
	9	4.16	2.76	3.4	3	0.27	A	100	1800
50	10	3.35	2.43	2.8	-	0.15	-	-	-
	11	2.8	2.4	2.6	-	0.14	-	-	-
	12	2.8	2.4	2.6	0.75	0.18	B	75	20
	13	2.8	2.4	2.6	2	0.26	B	75	20

d_n , d_v , d, ρ_{app}/ρ_{bulk}
method

have the same meaning as set forth above;
indicates the method employed, A or B, for admixing the flow enhancing additives

to the toner;
time indicates the time expressed in seconds during which the flow enhancing additives
are admixed with the toner particles according to either method A or B,
toner weight indicates the weight of the toner, expressed in g.;
5 conc. indicates the concentration of fumed silica added (Aerosil R812).

The particle size distribution of the toner with reference number 8 in the above Table 4 is set forth hereinafter.

10	Diam.	Vol % Dif.	<u>Table 5</u> Vol % Cum.
15	1.59	3.34	100.00
	2.00	5.82	96.66
	2.52	11.63	90.84
	3.19	21.38	79.21
20	4.01	28.14	57.83
	5.05	20.09	29.69
	6.36	7.58	9.60
	8.01	2.02	2.02
25	10.09	.00	.00

The columns two and three have the same meaning as the corresponding columns of Table 1. Analysis of
30 the size distribution shows the following results :
percentage of particles by volume larger than 3 micron : 82 %
percentage of particles by volume larger than 4 micron : 58 %
percentage of particles by volume larger than 5 micron : 31 %

The particle size distribution of the toner with reference number 13 in the above Table 4 is set forth hereinafter.
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50

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Table 6

	Diam.	Vol % Dif.	Vol % Cum.
5			
	1.59	9.51	100.02
10	2.00	21.93	90.51
	2.52	40.94	68.58
	3.19	22.98	27.64
15	4.01	3.27	4.66
	5.05	.26	1.39
	6.36	.12	1.13
	8.01	.08	1.01
20	10.09	.00	.93
	12.71	.31	.93
	16.01	.62	.62

The columns two and three have the same meaning as the corresponding columns of Table 1. Analysis of the size distribution shows the following results :

percentage of particles by volume larger than 3 micron : 38 %

percentage of particles by volume larger than 4 micron : 5 %

percentage of particles by volume larger than 5 micron : 1 %

With respect to the electrostatographic process the following aspects were evaluated :

cleaning problems of the photoconductive drum, caused by strongly adhering toner particles thereto, transfer efficiency of toner particles from the photoconductive drum to the paper substrate in the transfer station, fog on the paper substrate, quality of the magnetic brush, and overall fluidity and supply of the toner to the development station.

Of the above mentioned toner compositions, the toners with ref. number 7, 8, 9 and 13 showed overall good performance in respect of the abovementioned process characteristics. The toner particles with ref. numbers 10 and 11 showed insufficient performance for all of the above process characteristics whereas the toner composition with ref. number 12 exhibited bad performance in respect of toner fluidity, fog, cleaning, and medium performance in respect of quality of the magnetic brush, and transfer efficiency.

From the above it may be concluded that the ratio of bulk over apparent density is the critical factor for determining whether a particular toner composition shows good overall performance in an electrostatographic process.

It therefore is essential to combine both the packing specification, expressed as ratio of apparent over bulk density of the toner particles, and the particle size distribution as selection criterium in order to realize the aim of the invention i.e. the high image quality by dry xerographic toner development.

Similar experiments were done with other silica types showing different specific surface areas and methanol values and are shown in the table hereunder, and were combined with toner ref. N°. 2, at a concentration of 2% w/w. The app/ bulk values were determined showing that fulfillment of the condition that the product of the specific surface are (A m²/g) times the methanol value (B % V/V) is equal to or larger than 10.000 conforms the condition set forth in this patent for the ρ_{app}/ρ_{bulk} values, and confirms the realisation of over-all good quality and performance.

Table 7

	1	2	3	4	5
5	1	0.18	200	26.5	5300
	2	0.26	200	56	11200
	3	0.29	300	51.6	15480
10	4	0.31	380	59.8	22724
	5	0.18	130	39.8	5174
	6	0.20	200	38	7600
15	7	0.23	300	36.2	10860
	8	0.18	200	0.0	0
	9	0.19	200	24.2	4840
20	10	0.19	200	18.0	3600
	11	0.22	200	50.0	10000
	12	0.18	200	26.5	5300
	13	0.20	170	45.0	7650
25	14	0.20	300	7.5	2250

Column 1 indicates the experiment number, using various flow enhancing additives;

column 2 indicates the ratio ρ_{app}/ρ_{bulk} ;

column 3 indicates the specific surface area of the flow enhancing additive expressed in m²/g;

column 4 indicates the methanol value of the flow enhancing additive;

column 5 indicates the product of specific surface area times methanol value.

From the above table 7 it may be concluded that the realisation of good overall quality and performance merges from the coordination of a selection within particlesize distribution, packing specifications expressed as ratio of apparent over bulk density of the toner particles, whereby the realisation of such densities is the result of using flow enhancing additives fulfilling strict specifications with respect to product of specific surface area and methanol - value, yielding on the over-all realisation of the aim of the invention, i.e. the high image quality by dry xerographic toner development.

Claims

1. Dry electrostatographic toner particles suitable for use in the development of an electrostatic charge pattern, said toner particles having a classified particle size distribution wherein
 - more than 90 percent by volume of the toner particles have equivalent particle size diameters larger than 0.5 micrometer, and less than 7 micrometer, and
 - more than about 50 percent by volume of the toner particles have equivalent particle size diameters of less than about 5 micrometer, and
 - whereby said toner particles have on their surface fine inorganic microparticles acting as flow enhancing additives in a concentration of at least 0,1% w/w and at most 5% w/w, said fine inorganic microparticles being characterized by a product of specific surface area A (m²/g) times methanol value B (% V/V) fulfilling the relation.

$$A \times B > 10.000$$

and whereby the ratio of the apparent density over the bulk density of the toner particles satisfies the following equation :

$$\frac{\rho_{app}}{\rho_{bulk}} > 0.2$$

2. Dry electrostatographic toner particles according to claim 1, wherein more than 90 percent by volume of the toner particles have equivalent particle size diameters larger than 0.5 μm and less than 6 μm , and wherein more than about 50 percent by volume of the toner particles have equivalent particle size diameters of less than about 4 μm .
3. Dry electrostatographic toner particles according to claim 1, wherein more than 90 percent by volume of the toner particles have equivalent particle size diameters larger than 0.5 μm and less than 5 μm , and wherein more than about 50 percent by volume of the toner particles have equivalent particle size diameters of less than about 3 μm .
4. Dry electrostatographic toner according to claim 1 wherein the fine inorganic microparticles are coated with hydrophobic groups containing entities, resulting in a methanol value larger than 20.
5. Dry electrostatographic toner according to claim 1 wherein the fine inorganic microparticles have a specific surface area larger than 150 m^2/g .
6. Dry electrostatographic toner according to any of the preceding claims wherein the fine inorganic microparticles are fumed inorganics.
7. Dry electrostatographic toner particles according to claim 6 wherein said fumed inorganics are fumed silica which is present in an amount of at least 0.5 % by weight with respect to the toner weight.
8. Dry electrostatographic toner particles according to any of the preceding claims comprising a colorant dispersed or dissolved in the toner binder resin.
9. Dry electrostatographic toner particles according to any of the preceding claims wherein the toner particles contain a negative or positive charge control agent.
10. Dry electrostatographic toner particles according to any of the preceding claims wherein the toner particles are mixed with carrier particles for cascade or magnetic brush development of electrostatic charge pattern.

Patentansprüche

1. Trockene elektrostatische Tonerteilchen für den Einsatz bei der Entwicklung eines elektrostatischen Ladungsbildes, welche Tonerteilchen einen Verteilungszustand der klassierten Teilchen aufweisen, dadurch gekennzeichnet, daß
 - mehr als 90 Vol.-% der Tonerteilchen äquivalente Teilchengrößendurchmesser aufweisen, die größer sind als 0,5 μm und kleiner als 7 μm , und
 - mehr als ca. 50 Vol.-% der Tonerteilchen äquivalente Teilchengrößendurchmesser aufweisen, die kleiner sind als ca. 5 μm , und
 - wobei diese Tonerteilchen an ihrer Oberfläche feine, anorganische, als Fließmittelzutaten dienende Mikroteilchen in einer Konzentration von mindestens 0,1 Gew.-% und höchstens 5 Gew.-% aufweisen, welche feinen, anorganischen Mikroteilchen sich kennzeichnen durch ein Produkt aus der spezifischen Oberfläche A (m^2/g) mit dem Methanolwert B (Vol.-%), das die nachstehende Beziehung erfüllt:

$$A \times B > 10\,000$$

und wobei das Verhältnis der Rohdichte zu der Schüttdichte der Tonerteilchen der nachstehenden Beziehung entspricht:

$$\frac{\rho_{\text{Roh}}}{\rho_{\text{Schütt}}} > 0,2$$

2. Trockene elektrostatische Tonerteilchen nach Anspruch 1, dadurch gekennzeichnet, daß mehr als 90 Vol.-% der Tonerteilchen äquivalente Teilchengrößendurchmesser aufweisen, die größer sind als 0,5 μm und kleiner als 6 μm , und dadurch, daß mehr als ca. 50 Vol.-% der Tonerteilchen äquivalente Teilchengrößendurchmesser aufweisen, die kleiner sind als ca. 4 μm .

3. Trockene elektrostatische Tonerteilchen nach Anspruch 1, dadurch gekennzeichnet, daß mehr als 90 Vol.-% der Tonerteilchen äquivalente Teilchengrößendurchmesser aufweisen, die größer sind als 0,5 µm und kleiner als 5 µm, und dadurch, daß mehr als ca. 50 Vol.-% der Tonerteilchen äquivalente Teilchengrößendurchmesser aufweisen, die kleiner sind als ca. 3 µm.
4. Trockene elektrostatische Tonerteilchen nach Anspruch 1, dadurch gekennzeichnet, daß die feinen, anorganischen Mikroteilchen mit hydrophobe Gruppen enthaltenden Einheiten überzogen worden sind, infolge dessen der Methanolwert mehr als 20 beträgt.
5. Trockene elektrostatische Tonerteilchen nach Anspruch 1, dadurch gekennzeichnet, daß die feinen, anorganischen Mikroteilchen eine spezifische Oberfläche von mehr als 150 m²/g aufweisen.
6. Trockene elektrostatische Tonerteilchen nach irgendeinem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß die feinen, anorganischen Mikroteilchen anorganische Stoffe, die nach dem Hochtemperaturhydrolyseverfahren in einer Knallgasflamme hergestellt wurden (auf englisch : fumed), sind.
7. Trockene elektrostatische Tonerteilchen nach Anspruch 6, dadurch gekennzeichnet, daß diese anorganischen Stoffe, die nach dem Hochtemperaturhydrolyseverfahren in einer Knallgasflamme hergestellt wurden, nach dem Hochtemperaturhydrolyseverfahren in einer Knallgasflamme hergestellte Kieselsäure (auf englisch : fumed silica) sind, die in einer Menge von wenigstens 0,5 Gew.-%, bezogen auf das Tonergewicht, enthalten ist.
8. Trockene elektrostatische Tonerteilchen nach irgendeinem der vorstehenden Ansprüche, die einen in dem Tonerbindemittelharz dispergierten oder aufgelösten Farbstoff umfassen.
9. Trockene elektrostatische Tonerteilchen nach irgendeinem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß die Tonerteilchen einen Negativ- oder Positivladungsregler enthalten.
10. Trockene elektrostatische Tonerteilchen nach irgendeinem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß die Tonerteilchen mit Trägerteilchen für die Kaskaden- oder Magnetbürstenentwicklung elektrostatischer Ladungsbilder vermischt wurden.

Revendications

1. Des particules de toner électrostatographique sec pour le développement d'une image électrostatique de charge, ces particules de toner présentant une répartition granulométrique des particules classées caractérisée en ce que :
 - plus de 90 % en volume des particules de toner présentent des diamètres de grosseurs de particule équivalents supérieurs à 0,5 µm et inférieurs à 7 µm, et
 - plus d'environ 50 % en volume des particules de toner présentent des diamètres de grosseurs de particule équivalents inférieurs à environ 5 µm, et
 - où ces particules de toner présentent sur leur surface des microparticules inorganiques fines servant d'adjuvants améliorant l'écoulement dans une concentration d'au moins 0,1 % en poids et de 5 % en poids tout au plus, ces microparticules inorganiques fines étant caractérisées par un produit de surface spécifique A (m²/g) par valeur méthanol B (% en volume) correspondant à la relation suivante

$$A \times B > 10\,000$$
 et où le rapport entre la masse volumique apparente et la masse volumique non tassée des particules de toner satisfait à la relation suivante :

$$\frac{\rho_{app}}{\rho_{non\, tassée}} > 0,2$$
2. Des particules de toner électrostatographique sec suivant la revendication 1, caractérisées en ce que plus de 90 % en volume des particules de toner présentent des diamètres de grosseurs de particule équivalents supérieurs à 0,5 µm et inférieurs à 6 µm, et plus d'environ 50 % en volume des particules de toner présentent des diamètres de grosseurs de particule équivalents inférieurs à environ 4 µm.

3. Des particules de toner électrostatographique sec suivant la revendication 1, caractérisées en ce que plus de 90 % en volume des particules de toner présentent des diamètres de grosseurs de particule équivalents supérieurs à 0,5 μm et inférieurs à 5 μm , et plus d'environ 50 % en volume des particules de toner présentent des diamètres de grosseurs de particule équivalents inférieurs à environ 3 μm .
4. Des particules de toner électrostatographique sec suivant la revendication 1, caractérisées en ce que les microparticules inorganiques fines sont enrobées d'unités contenant des groupements hydrophobes ayant pour conséquence une valeur méthanol supérieure à 20.
5. Des particules de toner électrostatographique sec suivant la revendication 1, caractérisées en ce que les microparticules inorganiques fines présentent une surface spécifique supérieure à 150 m^2/g .
6. Des particules de toner électrostatographique sec suivant l'une quelconque des revendications précédentes, caractérisées en ce que les microparticules inorganiques fines sont une matière inorganique pyrogénée (fabriquée suivant le procédé d'hydrolyse à haute température dans une flamme oxyhydrique, en Anglais : fumed).
7. Des particules de toner électrostatographique sec suivant la revendication 6, caractérisées en ce que la matière inorganique pyrogénée est de la silice pyrogénée qui est contenue en une quantité d'au moins 0,5 % en poids par rapport au poids du toner.
8. Des particules de toner électrostatographique sec suivant l'une quelconque des revendications précédentes comprenant un colorant dispersé ou dissout dans la résine liante du toner.
9. Des particules de toner électrostatographique sec suivant l'une quelconque des revendications précédentes, caractérisées en ce que les particules de toner contiennent un agent de réglage de charge négative ou positive.
10. Des particules de toner électrostatographique sec suivant l'une quelconque des revendications précédentes, caractérisées en ce que les particules de toner et un support granuleux sont mélangés pour le développement en cascade ou le développement à la brosse magnétique d'images électrostatiques de charge.