



Europäisches Patentamt
European Patent Office
Office européen des brevets

Publication number:

**0 380 813
A1**

12

EUROPEAN PATENT APPLICATION

21 Application number: **89200192.6**

51 Int. Cl.⁵: **G03G 9/087**

22 Date of filing: **31.01.89**

43 Date of publication of application:
08.08.90 Bulletin 90/32

64 Designated Contracting States:
AT BE CH DE ES FR GB GR IT LI LU NL SE

71 Applicant: **AGFA-GEVAERT naamloze
vennootschap
Septestraat 27
B-2510 Mortsel(BE)**

72 Inventor: **Tavernier, Serge Martin
Bouwenstraat 40
B-2548 Lint(BE)**
Inventor: **Op de Beeck, Werner Jozef
Aspergeveld 65b
B-2850 Keerbergen(BE)**

54 **Dry electrophotographic toner composition.**

57 The invention relates to a toner composition consisting of fusible electrostatically attractable toner particles suitable for being fixed to paper by heat and pressure fusing. According to the invention an electrophotographic toner composition is disclosed comprising a colorant dispersed in a resin binder, wherein the binder consists for at least 75 % by weight of a mixture of at least one acidic binder resin having an acid number in the range of 4 to 40 mg KOH/g, and at least one basic binder resin having free amino groups in an amount equivalent with 4 to 40 mg KOH/g and being present in an amount of at least 10 % and at most 90 % by weight with respect to the acidic resin(s), the acidic binder resin and the basic binder resin being present at least partly in the form of an acid-base reaction product.

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Dry Electrophotographic toner composition

The invention relates to a toner composition consisting of fusible electrostatically attractable toner particles suitable for being fused to paper or other substrates as for example transparent film materials or an aluminium sheet, by heat- and pressure fusing.

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. In earlier days latent images were mainly developed using a liquid developer consisting of a colloidal system of charged colloidal particles in an insulating liquid. Nowadays the latent image is in most cases 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.

There are different types of fusing processes used for fusing a toner powder image to its support. Some are based upon fixation primarily on fusing by heat, other 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, four major types should be considered. The first is an oven heating process in which heat is applied by hot air over a wide portion of the support sheet, the second is a flash heating process in which heat is produced in the toner by absorption of light energy emitted by a flash lamp, the third is a radiation process wherein the support with the toner image is irradiated mainly by infrared-radiation, and the fourth is a heating process wherein the support with the toner image is simultaneously pressed and heated. The latter process is commonly called the heated roller fusing process.

In a common heat- and pressure fusing process 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 heat loss within the copy.

The last mentioned fusing process has been employed widely in low-speed as well as high-speed fusing systems, since a remarkably high thermal efficiency is obtained because the surface of the heating roller is pressed against the toner image surface of the sheet to be fixed. An additional advantage is the possibility to use colour-toners, since the energy absorption is independent from the wavelength. Moreover this fusing process allows double-sided copying, or so-called duplex printing.

The major and important drawback of this fusing process is the inherent danger of the occurrence of so-called offset-phenomena.

If the fuser roller provides too much thermal energy to the toner and paper, the toner will melt to a point where its melt cohesion and melt viscosity is so low that "splitting" can occur, and some of the toner is transferred to the fuser roller. When splitting does occur the toner which is taken up by the fuser roller is usually transferred to the copy sheet during the next turn of the roller, giving rise to the phenomenon of the so-called "hot offset", and this occurs in particular when there is inadequate release and/or (cleaning). Such release can be provided and is commonly provided by wetting the fuser roller directly or indirectly with silicone oil.

Too little thermal energy on the contrary results in poor adhesion of the toner to the paper resulting in poor fusing.

In this case the toner particles may fuse together and to the roller but they do not fix to the paper - especially since the thermal energy is delivered through the toner. The unfixed, fused toner particles will likewise be deposited onto the copy sheet during the next turn of the roller, resulting in what is called "cold offset".

In both cases, 'cold' as well as 'hot' offset, some toner will be transferred to the pressure roller during the lapse of time between subsequent paper feedings, giving additional contamination on the back of the copy.

In order to prevent as much as possible the above described toner offset and to achieve good fusing quality two kinds of measures are generally applied. First, the fuser roller is coated with an adhesive material such as silicone rubber, or is provided with a smooth coating of polytetrafluoroethylene resin having a very low friction coefficient and low adhesivity. Secondly the fuser roller is wetted with silicone oil directly or indirectly and a mechanical cleaning means can be provided, either by means of a scraper blade, a cleaning pad or cleaning web. In some cases the cleaning and wetting actions are combined.

Although such actions prevent toner offset to a certain extent, a completely satisfactory result can only be obtained when the visco-elastic properties of the toner material itself are optimised for each envisaged application.

Toner properties should in fact be optimised i.a. in function of the following characteristics :

- 5 - speed of the overall electrophotographic process, ranging from the high-speed copying apparatus (e.g. 60 copies per minute, where copying speed is of major importance) to the relatively slower laser-printer apparatus where quality of the resulting print is a primary aim (e.g. 12 copies per minute);
 - the type of the envisaged electrophotographical development :
 - concept of development : monocomponent, conductive or insulating type, dual component;
 - 10 - polarity of the toner resp. carrier particles;
developing a positive replica of the electrostatic image or a reversal replica.
- Further in particular the visco-elastic properties of the toner should be adjusted in function of the envisaged fusing process : heat roller fusing method, oven heating process, flash heating process or any other fusing method.

- 15 For each particular application a specific toner composition should thus be optimised. This optimization implies in the first place the determination of the most appropriate type of toner-binder and the determination of the most appropriate molecular weight distribution of the binder resin selected.

Once the binder resin has been selected, the following parameters further should be adjusted :

- weight proportion of the selected binder composition in the overall toner-composition;
- 20 - possible addition of release promoting agents such as waxy resins or fatty acid derivatives particularly suitable for preventing toner offsetting; in particular the addition of waxy polyalkylene resins can be considered;
- type and polarity of charge control agent;
- type of colorant selected;
- 25 - etc.

The development and manufacture of a large number of specific toner compositions, each of which having been optimised in function of the particular characteristics of a given electrophotographic application, implies substantial practical disadvantages. In particular the selection of various binder resins causes a lot of extra work.

- 30 Indeed, such a procedure implies the need of sourcing or synthesising some particular compounds not commonly available on the market and which may be particularly useful for some applications; the obligation of keeping a stock of all chemical compounds used in each particular toner composition; the need to apply quality control on each of these raw materials for the various toner preparations; the obligation of regularly varying the manufacturing parameters for each toner composition, etc.

- 35 Further, if a particular binder resin can be obtained from a supplier, a second supplier, so-called second source, should preferably be found in order to assure the continuous delivery of such binder resin.

- It is therefore an object of the present invention to develop dry electrophotographic toner compositions with varying visco-elastic properties and/or polarity as imposed by various electrophotographic applications which may be manufactured on the basis of one and the same resin-combination, acting as binding agent;
- 40 the latter implies that e.g. a change in polarity of a toner may be achieved only by selecting another charge control agent, the binding agent system remaining unchanged.

Other objects and advantages will become apparent from the hereinafter following description and examples.

- In accordance with the present invention, a dry electrophotographic toner composition suitable for use
- 45 in the development of electrostatic charge patterns comprising a colorant dispersed or dissolved in a resin binder, has now been developed characterized in that the binder consists for at least 75 % by weight of a mixture of at least one acidic binder resin, having an acid number in the range of 4 to 40 mg KOH/g, and at least one basic binder resin having free amino groups in an amount equivalent with 4 to 40 mg KOH/g and being present in an amount of at least 10 % by weight and at most 90% by weight with respect to the
- 50 acidic resin(s), the acidic binder resin and the basic binder resin being present at least partly in the form of an acid-base reaction product.

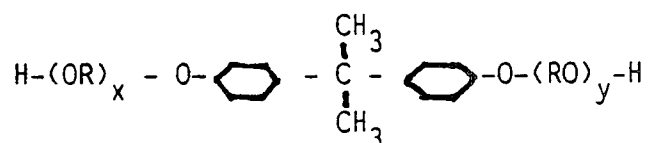
- Examples of acidic binder resins suitable for use according to the present invention are : addition or condensation polymers having groups of acidic nature such as carboxylic acid groups, sulphonic acid groups and phenol-type hydroxy groups. More particularly are mentioned vinyl type addition polymers
- 55 possessing in their structure said acidic groups introduced by (random) copolymerization or graft-copolymerization, e.g. copolymers of lower alkyl esters of acrylic acid and/or styrene with unsaturated acids such as acrylic acid, methacrylic acid, maleic acid and itaconic acid or copolymers of butadiene wherein the mentioned groups of acidic nature have been introduced by graft-copolymerization.

Preferred acidic condensation polymers for use according to the present invention are acidic polyester resins, e.g. those produced by the condensation reaction of a polyol or mixture of polyols, e.g. ethylene glycol, triethylene glycol and an alkoxyated bisphenol especially bisphenol A, i.e. [2,2-bis(4-hydroxyphenyl)-propane], with a dicarboxylic acid or mixture of dicarboxylic acids, e.g. maleic acid, fumaric acid, itaconic acid, malonic acid, isophthalic acid and optionally partly with a polyacid having at least 3 carboxylic acid groups such as trimellitic acid yielding some crosslinking.

The preparation of linear polyester resins of the above type is described in GB-P 1,373,220.

A particularly useful acidic polyester binder is derived from terephthalic acid that is polycondensed with less than 1 equivalent of an ethoxylated and/or propoxylated "bisphenol A".

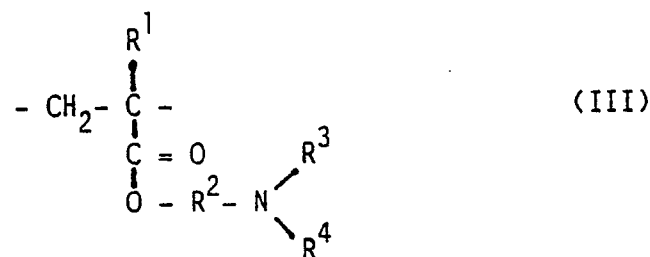
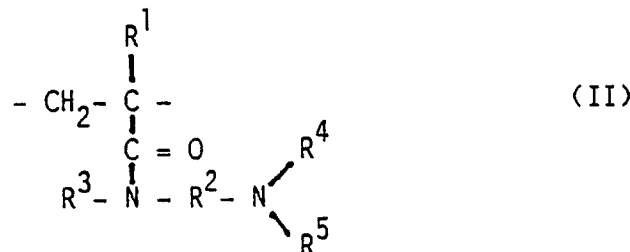
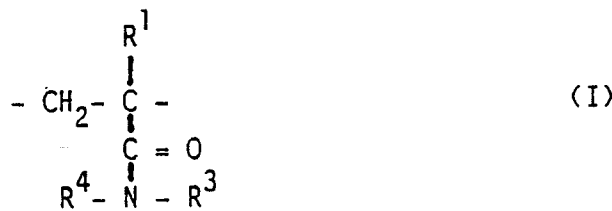
The synthesis of partly crosslinked polyesters for use in accordance with the present invention is described e.g. in published GB-2082788A patent application disclosing toner comprising as a binder a polyester resin obtained from a diol or mixture of diols represented by the following general formula :



wherein R represents an ethylene or propylene group, x and y are independent numbers such that the average value of their sum is 2 to 7; and a polycarboxylic acid or a derivative thereof, which is a mixture of a dicarboxylic acid or a C₁₋₆ alkyl ester thereof and a tri- or polycarboxylic acid or an acid anhydride thereof, the content of said tri- or polycarboxylic acid or acid anhydride being from 30 to 80 mol% of the acids.

Alkaline or basic polymers suited for use according to the present invention contain free amino groups in an amount at least equivalent with 4 mg of KOH per gram and up to 40 mg of KOH per gram. These polymers are e.g. vinyl type addition polymers containing free amino groups, polyethyleneimine, condensation polymers of the polyamide type having an excess of free amino groups and amino-aldehyde resins, e.g. melamine-formaldehyde resins having an excess of free amino groups.

Particularly useful basic addition polymers are homo- or copolymers including monomer units corresponding to one of the following structural formulae (I), (II) or (III) :



wherein :

- R^1 represents hydrogen or methyl,
 R^2 represents a bivalent hydrocarbon group, e.g. an alkylene group having from 1 to 12 carbon atoms, and
 R^3 , R^4 and R^5 - same or different - represent hydrogen or a hydrocarbon group, e.g. a C1-C12 hydrocarbon group.

The useful basic addition polymers referred to include one of said monomer units preferably in an amount of at least 1% by weight.

Monomers of the above type and their polymerization are described in detail in US-P 4,020,192. Preferred examples of said addition polymers contain monomer units according to the above general formula (III) such as methyl methacrylate ester of N,N'-dimethyl ethanolamine.

In copolymers including at least one of said monomer units other monomer units are e.g. styrene and styrene homologues, acrylate and methacrylate esters, acrylamide, acrylonitrile, methacrylonitrile, vinyl chloride and vinyl acetate.

For further optimizing the toner properties in admixture with the above defined copolymer(s) other resins or pigments modifying the melt viscosity and/or release agents assisting in the release of the toner melt from the fuser roller may be used. 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-P 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 dyestuff pigment 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.

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), ferric oxide (Fe_2O_3 = hematite) and ferrosferric oxide (Fe_3O_4 = magnetite), cupric oxide; other magnetic or magnetizable pigments than the latter two iron oxides can also be used.

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.

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).

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.

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 NO4 (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.

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 to an average particle size of 1 to 100 microns. Preferably the fraction having a particle size between 5-20 μm is used.

In order to improve the flow properties of the toner the toner particles may be admixed with a metal soap e.g. zinc stearate as described e.g. in the United Kingdom Patent Specification No. 1,379,252. The preferred proportions of metal soap such as zinc stearate to toner material are in the range of 0.05 to 1 % by weight. For the same purpose colloidal silica may be used, alone or in addition to the metal soap. The use of silica as flow improving agent for toner compositions is described in the United Kingdom Patent Specification No. 1,438,110.

The colloidal silica particles used in the developer composition according to the present invention are preferably free from pores i.e. have a smooth substantially spherical surface. Their specific surface area is preferably in the range of 100 to 400 sq.m/g .

Colloidal silica particles suitable for use according to the present invention are commercially available under the Trade Name KIESELSOL 500 (KIESELSOL is a registered trade name of Farbenfabriken Bayer AG, Leverkusen, West-Germany), 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 300 is a colloidal silica having a specific surface area of 300 sq.m/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. 8 (1958) 1387-1390.

The preferred proportions of colloidal silica to toner material are in the range of 0.1 to 0.5 % by weight.

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 e.g. with carrier particles or applicator used.

The toner compositions of the present invention may be used as monocomponent toners or they can 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, if such are employed, 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.

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-P 4,600,675. Many of the foregoing and typical carriers are disclosed in U.S.Pat. Nos. 2,618,441; 2,638,416; 2,618,522; 3,591,503 and 3,533,835 directed to electrically conductive carrier coatings, and U.S.Pat. No. 3,526,533 directed to polymer coated carriers. Oxide coated iron powder carrier particles are described e.g. in U.S.Pat.No. 3,767,477. The U.S.Pat.No. 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.

The present toner composition when containing a magnetically attractable pigment can be used for magnetic brush monocomponent development of electrostatic charge patterns as well as for the development of latent magnetic images.

Magnetic materials suitable for said use are magnetic or magnetizable metals including iron, cobalt, nickel and various magnetizable oxides including (hematite) 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 any of these. Good results can be obtained with about 30 % to about 80 % by weight of magnetic material with respect to the resin binder of the toner.

The development of latent magnetic images is described e.g. in U.S.Pat.No. 4,271,248 wherein a magnetically attractable toner is described. Hot roll fusing of monocomponent toners is described e.g. in Journal of Imaging Technology, Vol. 11, No. 6, Dec. 1985, p. 261-279.

For fixing a toner image to a sheet or web support, e.g. a paper sheet, the above described toner after being deposited in image configuration on said support is conveyed between means that exert substantially equal pressure on the front and rear side of said support, while at least the means directed to the front side and contacting the toner particles is at a temperature sufficient to fuse the toner particles and has a surface with highly adhesive character, and smooth surface.

In a preferred embodiment said toner-image bearing support is conveyed through the nip formed by rollers rotating in opposite direction, wherein the roller contacting the toner image contains a heating source e.g. infra-red radiator or electrical resistance heating element. In most apparatus for providing the necessary pressure a spring pressure mechanism is used actuating the pressure roller which is a support roller contacting the rear side of the toner-image bearing support. An example of a preferably used toner fixing apparatus containing a fuser and pressure roller with self-adjusting pressure mechanism is described in the

United States Patent Specification 4,269,594. Other roller fusing devices for fixing toner images are provided with a pneumatically operated bladder to apply an equal pressure to all toner image parts. Examples of such devices are disclosed in Research Disclosure September 1981 items 20904, 20906 and 20914.

In an embodiment for carrying out the present heat and pressure fixing process on non-metal supports, e.g. paper supports, the fuser roller consists of a tube in aluminium or stainless steel having e.g. an inner diameter of 40 to 45 mm, a wall thickness of 1 to 2 mm and a length of 230 mm onto which a layer of polytetrafluorethylene with a thickness of 20 to 60 μm is provided. Within the tube, and centrally located is provided a 500 to 1000 Watt halogen flood light lamp. This type of lamp enables the fuser roller to attain a surface temperature of about 180 °C in standby position. The pressure roller acting as support roller co-operating with said fuser roller is a solid cylinder of stainless steel, copper or aluminium that may be internally heated and onto which a layer of silicone rubber with a thickness in the range of 3 to 10 mm having a Shore A hardness in the range of 30 to 60 has been applied.

The pressure roller and the heat fuser roller are mounted in contact with each other and the pressure at the area of contact with the toner is adjusted at a value in the range of 1 to 2 kg per cm of the tangent line between the rollers. Operating with the above rollers under the above circumstances of pressure a tangent line with a width in the range of 5 to 9 mm is obtained. The pressure between the fuser and pressure roller can be controlled by spring(s) or pneumatically.

According to a preferred embodiment the fuser roller is cleaned with a web, e.g. porous paper web, impregnated with silicone oil.

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

In these examples reference is made to polymers A, B, C, D and E the details of which are set forth hereinafter :

Polymer A

A reference binder, produced by statistical addition polymerisation of styrene and n-butylmethacrylate (80/20) having an acid number of 1 mg KOH/g, due to small amounts of methacrylic acid caused by spontaneous hydrolysis, a glass transition temperature of 62 °C, and a melt index of 10 g/10' determined at 160 °C and 2.16 kg load. All melt indices set forth in this application are determined in accordance with the Standard Test Method for Flow rates of thermoplastics by extrusion Plastometer, reference ASTM-designation D1238-82.

Polymer B

A basic binder resin, produced by statistical addition polymerisation of styrene, 2-ethylhexyl acrylate and 1-dimethylamino-ethyl methacrylate (79/20/1) having an alkalinity equivalent with 5,1 mg KOH/g, a glass transition temperature of 58 °C, a melt-index of 3 g/10' at 160 °C and 2.16 kg load.

Polymer C

An acidic binder resin, produced by condensation reaction of propoxylated bisphenol A, i.e. [2,2-bis(4-hydroxyphenyl)-propane], with fumaric acid.

This binder resin is characterised by an acid number of 12,8 mg KOH/g, a melt index of 12 g/10' at 105 °C and 2.16 kg load, and a glass transition temperature of 56 °C.

Polymer D

An acidic binder resin, produced by condensation reaction of propoxylated bisphenol A, i.e. [2,2-bis(4-hydroxyphenyl)-propane], with terephthalic acid and trimellitic acid according to the preparation described in GB-P 1,373,220 or published GB-2082788A patent application.

This binder resin is characterised by an acid number of 18,0 mg KOH/g, a melt index of 40 g/10' at 160 °C and 2.16 kg load, and a glass transition temperature of 64 °C.

Polymer E

An acidic binder resin, produced by statistical addition polymerisation of styrene, n-butylmethacrylate and methacrylic acid (80/20/x) was prepared and characterised by an acid value of 14 mg KOH/g, a glass transition temperature of 55° C and a melt index of 24 g/10' at 160° C and 2.16 kg load.

COMPARATIVE EXAMPLE 1

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Toner preparation

90 parts of polymer A, 2 parts of SPILON BLACK TRH (being a Cr-azo-naftol-derivative, trademarked product of HODOGAYA Chemical Co. Ltd., 4-2 Toranomon, 1-chome, Minato-ku, Tokyo 105, Japan) as negative charge controlling agent, 2 parts of VISCOL 660 P release agent (a trademarked product of Sanyo Chemical Industries Ltd., No. 10 Chuo Bldg., 9, Honcho 1-chome, Nihonbashi, Chuo-ku, Tokyo 103, Japan, being an isotactic polypropylene, melting point : $T_m = 145^{\circ}\text{C}$), and 8 parts of Cabot Regal 400 (a trademarked product of Cabot, being a carbon black) were introduced in a kneader and heated at 145° 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. The powder obtained was further reduced in grain size by jet milling to obtain an average particle size of 12 μm , the portion with particle size smaller than 5 μm , and the portion with particle size greater than 20 μm each being below 2 percent by weight.

To improve the flow properties of the toner 0.3 parts of colloidal silica (Aerosil R972, a trademarked product of Degussa AG, Germany) were admixed thereto.

30 Development and Transfer

An electrostatic image formed on an electrophotographic recording element (i.e. an organic photoconductor coated conductive drum, which was negatively 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 uncoated iron bead carrier of approximately 75 μm diameter particles in a concentration of 5 wt % with respect to the total weight of carrier.

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.

40

Fixation - characterisation :

The image-wise transferred toner particles were fed to a heat-and-pressure roller fixing device.

In said device the fuser roller consisted of a tube in stainless steel having an inner diameter of 41 mm, a wall thickness of 1.2 mm and a length of 230 mm onto which a layer of silicone rubber with a thickness of 1.0 mm was provided. Within the tube, and centrally located was provided a 1000 Watt halogen flood light lamp. This lamp enables the fuser roller to attain a surface temperature of 210° C in standby position. The pressure roller acting as support roller co-operating with said fuser roller was a solid cylinder of stainless steel onto which a layer of silicone rubber with a thickness of 7 mm was provided. The diameter of the roller was 44 mm. The pressure roller was cleaned from paper dust by contacting it with a silicone-oil impregnated wick.

The pressure roller and the heat fuser roller were mounted in contact with each other and the pressure at the area of contact with the toner is adjusted at a value of 0.7 kg per cm tangent line between the rollers.

The pass-through speed of the receiving paper carrying the toner image was 8 cm/s and the surface temperature of the heating roller was set at 180° C.

For the assessment of the degree of fixation a "folding test" was carried out.

In the test procedure a solid black area of deposited toner (1 mg/cm²) is folded, the folded edge being

compressed between two metal rollers with nip loading operating as follows :
travelling speed : 20 cm/s,
pressure : free weight of the upper roller 600 g + weight of the ball bearings : 40 g.
width : 10 cm.

5 Hereafter, the paper is unfolded and the solid black area is then rubbed with common copying paper used in xerography under the following conditions :
friction pressure : 50 g/cm²
friction velocity : 0.15 m/s
number of rub streaks : 5.

10 The fixation degree is defined as the ratio of optical densities (D2/D1) measured on the folded and friction-treated black area over the optical density of the black area of the non-folded paper. A density ratio (D2/D1) of 0.8/1 is considered to correspond with a high fixation degree.

The degree of fixation was determined by this procedure at a temperature of 180 °C and yielded 0.92, corresponding to a very good fixing rate. However the hot-offset became apparent at 185 °C and higher. If
15 the toner was used in a higher speed system (18 cm/sec) the fixation reached only 0.75 and hot-offset occurred at higher temperatures (205 °C).

Charge-characterisation :

20 The charge of the toner within the described developer was determined using standard blow-off techniques by means e.g. of the blow-off type powder charge measuring apparatus marketed by Toshiba Chemical Products Co. Ltd., 3-9, Shimbashi 3-chome, Minato-ku, Tokyo 105, Japan. The charge of the described toner was measured and found to be - 8 uC/g. This value is satisfactory since values of at least
25 + or - 2 uC/g are preferred. Toners characterized by values situated between -2 and +2 uC give mixing problems with the carrier and badly mixed developer gives rise to background deposition on the copy.

COMPARATIVE EXAMPLE 2

30 Analogously to the procedure of Comparative Example 1, a toner was prepared; however 4 parts of BAYSCRIPTONER GBA-CCA (product of Bayer AG, Germany, being a positive charge controlling agent), 2 parts of VISCOL 660P and 6 parts of CABOT REGAL 400 were used.

35 The mixing of this toner with carrier particles yielded a useful electrophotographic developer combination with similar fusing behaviour and a tribo-electric charge determined by conventional blow-off methods of + 6 uC/g.

COMPARATIVE EXAMPLE 3

40 Analogously to the procedure of Comparative Example 1, a toner was prepared with the difference however that polymer A was replaced by polymer B. No useful developer was obtained as the tribo-electric
45 charge of the toner mixed with said carrier was so low that a dusty mixture was obtained (the tribo-electric charge determined by conventional blow-off methods was less than 1 uC/g).

COMPARATIVE EXAMPLE 4

50 Analogously to the procedure of Comparative Example 2, a toner was prepared with the difference however that polymer A was replaced by polymer D. No useful developer was obtained as the tribo-electric
55 charge of the toner mixed with said carrier was so low that a dusty mixture was obtained (the tribo-electric charge determined by conventional blow-off methods was less than 1 uC/g).

EXAMPLE 1a

Analogously to the procedure of the Comparative Examples 1 and 3, a toner was prepared with the difference however that a resin of the following composition was used as binding agent : 35 parts of the polymer B and 55 parts of the polymer D.

Use of the negative charge-controlling agent as described in said comparative example 1, yielded toner particles with a negative tribo-electric charge, which when determined by conventional blow-off methods turned out to be -3.3 uC/g; a broad fusing window in both slow and high speed systems was found; hot offset occurred above 210 °C and the fusing degree at 180 °C was above 0.8 for both systems.

EXAMPLE 1b

The toner preparation of Example 1a was repeated with the difference however that the positive charge-controlling agent as described in comparative example 2 was used at 4 % concentration, with carbon black at 6 % concentration; this procedure yielded toner particles with a positive tribo-electric charge, which when determined by conventional blow-off methods turned out to be +2.8 uC/g. The fusing characteristics were similar as those for Example 1a.

EXAMPLE 1c

The toner preparations of the Examples 1a and 1b were repeated with the difference however that the two polymers B and D were mixed beforehand in a 50/50 weight proportion and were allowed to react during a melt kneading process so that acid-base reactions could take place, and that this already cross-linked polymer matrix was used as binder resin in the toner preparation step. No difference in performance compared to the examples 1a and 1b was noticed. It should be noted that the reaction product was a clear binder. This stresses the effect of the occurring acid-base reaction so as to increase the compatibility between both binders.

EXAMPLE 2a

Analogously to the procedure of Example 1a, a toner was prepared with the difference however that a resin of the following composition was used as binding agent : 45 parts of polymer B and 45 parts of polymer E.

Use of the negative charge-controlling agent as described in comparative example 1 yielded toner particles with a negative tribo-electric charge which when determined by conventional blow-off methods, turned out to be -4.1 uC/g. The fusing characteristics were similar as those for Example 1a.

EXAMPLE 2b

The toner preparation of Example 2a was repeated with the difference however that the positive charge-controlling agent as described in comparative Example 2 was used at 4 % concentration, with carbon black at 6 % concentration; this procedure yielded toner particles with a positive tribo-electric charge, which when determined by conventional blow-off methods turned out to be +6.7 uC/g. The fusing characteristics were similar as those for Example 1a.

EXAMPLE 2c

The toner preparation of Example 2b was repeated with the difference however that no release agent

was used. No deterioration of the hot offset characteristics were observed.

EXAMPLE 3

Analogously to the procedure of Example 1b, a toner was prepared with the difference however that a resin of the following composition was used as binding agent : 45 parts of polymer B and 45 parts of polymer C.

Use of the positive charge-controlling agent as described in comparative example 2 yielded toner particles with a positive tribo-electric charge which when determined by conventional blow-off methods, turned out to be +3.0 uC/g. Good fusing properties were observed.

The polymer C is a resin which typically is to be used in flash-fusing or radiation fusing apparatus. Hence, the above example illustrates that the coupling of different copolymers by the occurrence of acid-base reactions may yield resins with visco-elastic properties which may specifically be designed towards the envisaged electrophotographic application. More in particular the above example illustrates that a resin with visco elastic properties specifically adapted for a flash fusing system may also be used for a heated roller fusing system, provided it is reacted with another polymer so that the visco-elastic properties of the resulting polymer are suited for the envisaged heated-roller fusing system.

Claims

1. A dry electrophotographic toner composition suitable for use in the development of electrostatic charge patterns comprising a colorant dispersed or dissolved in a resin binder, wherein the binder consists for at least 75 % by weight of a mixture of at least one acidic binder resin having an acid number in the range of 4 to 40 mg KOH/g, and at least one basic binder resin having free amino groups in an amount equivalent with 4 to 40 mg KOH/g and being present in an amount of at least 10 % and at most 90 % by weight with respect to the acidic resin(s), the acidic binder resin and the basic binder resin being present at least partly in the form of an acid-base reaction product.

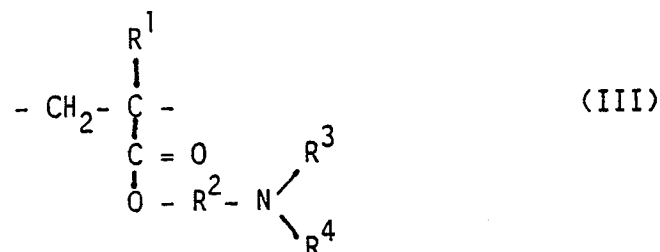
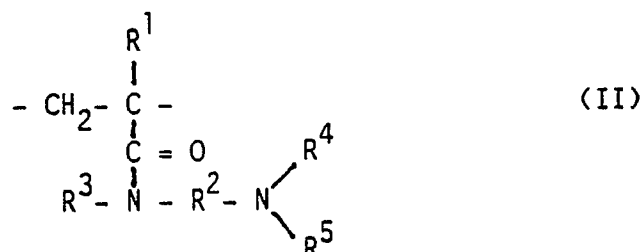
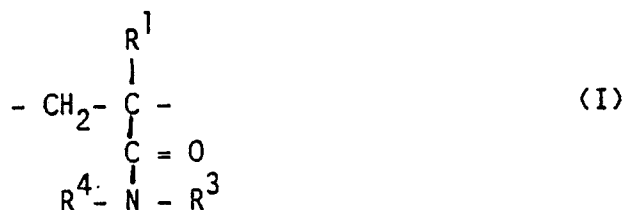
2. A dry electrophotographic toner composition according to claim 1, wherein the said acidic binder resin is an addition or condensation polymer having acidic groups selected from the group consisting of carboxylic acid groups, sulphonic acid groups and phenol-type hydroxy groups.

3. A dry electrophotographic toner composition according to claims 1 or 2, wherein the said acidic resin binder is an acidic polyester resin produced by the condensation reaction of a polyol or mixture of polyols with a dicarboxylic acid or mixture of dicarboxylic acids and optionally partly a polyacid having at least 3 carboxylic acid groups yielding some crosslinking.

4. A dry electrophotographic toner composition according to claim 3, wherein the acidic polyester binder is derived from terephthalic acid that is polycondensed with less than 1 equivalent of an ethoxylated and/or propoxylated "bisphenol A".

5. A dry electrophotographic toner composition according to any of the preceding claims, wherein the said basic addition polymer is selected from the group consisting of vinyl type addition polymers containing free amino groups, polyethyleneimine, condensation polymers of the polyamide type having an excess of free amino groups and amino-aldehyde resins having an excess of free amino groups.

6. A dry electrophotographic toner composition according to claim 5, wherein the said basic addition polymer is a homo- or copolymer including monomer units corresponding to one of the following general formulae (I), (II) or (III):



wherein :

30 R^1 represents hydrogen or methyl,

R^2 represents a bivalent hydrocarbon group, and

R^3 , R^4 and R^5 - same or different - represent hydrogen or a hydrocarbon group.

7. A dry electrophotographic toner composition according to any of claims 1 to 6, wherein the toner particles contain a magnetic or magnetizable pigment.

35 8. A dry electrophotographic toner composition according to any of claims 1 to 7, wherein said resin binder in order to bring the melt viscosity of the toner in the desired range is used in admixture with a viscosity regulating pigment.

9. A dry electrophotographic toner composition according to any of claims 1 to 8, wherein the said colorant is carbon black.

40 10. A dry electrophotographic toner composition according to any of claims 1 to 9, wherein the toner particles contain a negative or positive charge control agent.

11. A dry electrophotographic toner composition according to any of claims 1 to 10, wherein the toner particles are mixed with carrier particles for cascade or magnetic brush development of electrostatic charge patterns.

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	PATENT ABSTRACTS OF JAPAN, vol. 7, no. 212 (P-224)[1357], 20th September 1983; & JP-A-58 107 549 (CANON K.K.) 27-06-1983 * Abstract * ---	1-11	G 03 G 9/087
X	EP-A-0 066 395 (XEROX) * Abstract; page 3, paragraph 2 - page 5, paragraph 3; page 6, paragraphs 3,4; page 8, paragraph 6 - page 10, paragraph 4; claims * ---	1-11	
A	GB-A-1 352 804 (KONISHIROKU) * Page 2, line 66 - page 2, end; claims * ---	5,6	
D,A	GB-A-2 082 788 (KONISHIROKU) * Claims * -----	3,4	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G 03 G
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 27-09-1989	Examiner VANHECKE H.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	