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(54) Dry toner particles having controlled charging properties

(57) Dry toner particles containing both a charge control agent (CCA) and a charge limitation agent (CLA). Preferably the CLA is a meso-ionic compound. The particles exhibit an acceptable speed of triboelectric charging, a narrow charge distribution and a charge stability that is retained for long printing times.

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Description

Field of the invention

[0001] This invention relates to dry toner particles for use in electrostatographic printing systems. In particular it relates to dry toner particles with adapted charging properties.

Background of the invention

[0002] It is well known in the art of electrostatography including electrography and electrophotography to form an electrostatic latent image either corresponding to the original to be copied, or corresponding to digitised data describing an electronically available image.

[0003] In electrophotography an electrostatic latent image is formed by the steps of uniformly charging a photoconductive member and image-wise discharging it by an image-wise modulated photo-exposure.

[0004] In electrography an electrostatic latent image is formed by image-wise depositing electrically charged particles, e.g. electrons or ions onto a dielectric substrate.

[0005] The obtained latent images are developed, i.e. converted into visible images by selectively depositing thereon light absorbing particles, called toner particles, which are charged.

[0006] Also, charged toner particles are used in the process of Direct Electrostatic Printing (DEP), in which an image is created upon a receiving substrate by creating a flow of charged toner particles from a toner bearing surface to the image receiving substrate and image-wise modulating the flow of toner particles by means of an electronically addressable printhead structure.

[0007] In any of the electrostatographic techniques using charged dry toner particles, it is important that the charge is evenly distributed over all particles, i.e. that the charge distribution is narrow. A broad distribution of charge is characterised by (1) the presence of a relatively large amount of particles that have a charge too low for providing a sufficiently strong coulomb attraction and (2) the presence of wrong charge sign toner particles that have a charge sign opposite to the major part of the bulk of the toner particles. The development with such kind of developer results in an undesirable image-background fog.

[0008] Charging of the individual toner particles through triboelectricity (frictional contact between triboelectric partners) is a statistical process which will result in a broad distribution of charge over the number of toner particles in the developer if no proper measures of charge control are taken. In e.g. United States patents US-A-5 532 097, US-A-5 569 567 and US-A-5 622 803, means and ways are described to provide toner particles with a narrow charge distribution.

[0009] Not only the charge distribution has to be controlled in toner particles, but also the speed of charging and the stability of the charge during the printing time.

[0010] It is an object of the invention to provide dry toner particles having an acceptable speed of tribo-electric charging and the stability of the charge which is retained for long printing time, ideally combined with a narrow charge distribution.

SUMMARY OF THE INVENTION

[0011] We have now discovered that this object, and other useful benefits, can be achieved by providing dry toner particles containing both a charge control agent (CCA) and a charge limitation agent (CLA).

[0012] The toner particles of this invention can further incorporate any ingredient known in the art, e.g., toner resin, one or more colorants, metal oxides.

[0013] The toner particles of this invention can be toner particles with a negative charge as well as toner particles with a positive charge. When toner particles with a negative charge are needed, charge control agents for inducing or enhancing a negative chargeability are used. Charge control agents are well known in the art of preparation of toner particles.

[0014] For toner particles with a positive charge, mainly ammonium compounds, pyridinium compounds, triphenylmethane, cationic dyes, negrosine dyes, etc. are used. Charge control agents for positive charging are commercially available through e.g. Ciba-Geigy of Switzerland under trade name CG 14-146, CG 16-569, BASF of Germany under trade name NEPTUNSCHWARZ X60, Orient Chemical of Japan under trade name BONTRON P51.

[0015] For toner particles with negative charge, mainly metal complexes, phenylsilicates, naphthylsilicates, azo compounds, cationic polymers, modified ammonium compounds etc. are used. Charge control agents for negative charging are commercially available through e.g. Clariant of Germany under trade name NCS LP 2145, NCS VP 2145, COPY CHARGE NCA, Orient Chemical of Japan under trade name BONTRON E82, BONTRON S34, BONTRON S44, BONTRON F21.

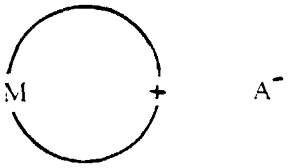
[0016] The charge control agent (CCA) can be present in any concentration known in the art, an amount between

0.5 and 5% by weight of the CCA being preferred.

[0017] The charge limitation agent (CLA) used in toner particles of this invention is most preferably selected from meso-ionic compounds.

[0018] Meso-ionic compounds as referred to in the present invention are a group of compounds defined by W. Baker and W.D. Ollis as "5- or 6-membered heterocyclic compounds which cannot be represented satisfactorily by any one covalent or polar structure and possesses a sextet of p-electrons in association with the atoms comprising the ring. The ring bears a fractional positive charge balanced by a corresponding negative charge located on a covalently attached atom or group of atoms" as described in Quart. Rev., Vol. II, p. 15 (1957) and Advances in Heterocyclic Chemistry, Vol. 19, P. 4 (1976). Preferred meso-ionic compounds are those represented by formula (I):

(I)

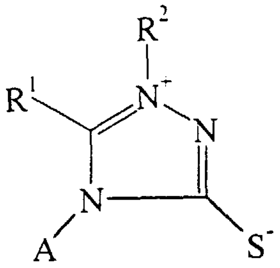


wherein M represents a 5- or 6-membered heterocyclic ring composed of at least one member selected from the group consisting of a carbon atom, an oxygen atom, a sulphur atom and a selenium atom; and A$^-$ represents -O$^-$, -S$^-$ or -N$^-$-R, wherein R represents an alkyl group (preferably having 1 to 6 carbon atoms), a cycloalkyl group (preferably having 3 to 6 carbon atoms), an alkenyl group (preferably having 2 to 6 carbon atoms), an alkynyl group (preferably having 2 to 6 carbon atoms), an aralkyl group, an aryl group (preferably having 6 to 12 carbon atoms), or a heterocyclic group (preferably having 1 to 6 carbon atoms).

[0019] In formula (I), examples of the 5-membered heterocyclic ring as represented by M include an imidazolium ring, a pyrazolium ring, an oxazolium ring, an isoxazolium ring, a thiazolium ring, an isothiazolium ring, a 1,3-dithiol ring, a 1,3,4- or 1,2,3-oxadiazolium ring, a 1,3,2-oxathiazolium ring, a 1,2,3-triazolium ring, a 1,3,4-triazolium ring, a 1,3,4-, 1,2,3- or 1,2,4-thiadiazolium ring, a 1,2,3,4-oxatriazolium ring, a 1,2,3,4-tetrazolium ring and a 1,2,3,4-thiatriazolium ring.

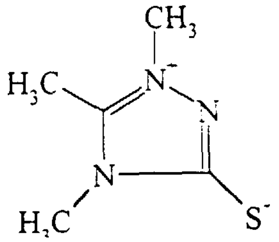
[0020] Meso-ionic compounds are known for use in the fixing step of a photographic process as disclosed in European patent specification EP-A-431 568. Triazolium thiolate meso-ionic compounds are well known in silver halide photography and are used for increasing temperature latitude as disclosed in Japanese patent specification JP-A-60-117240, for reducing fog as disclosed in United States patent US-A-4 615 970, in preparing silver halide emulsions as disclosed in United States patent US-A-4 631 253, in bleach etching baths as disclosed in European patent specification EP-A-321 839, to prevent pressure marks as disclosed in United States patent US-A-4 624 913, and in European patent specification EP-A-554 585 for enhancing the printing properties and especially the printing endurance of a lithographic printing plate according to the DTR process.

[0021] Preferred meso-ionic compounds for use in toner particles useful in the method of this invention correspond to the formula :

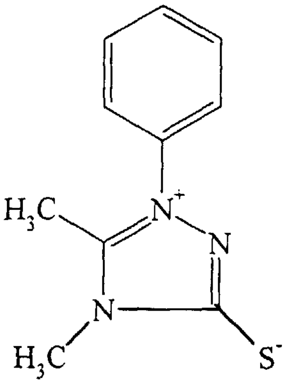


wherein R^1 and R^2 each independently represents an unsubstituted or substituted alkyl group, alkenyl group, cycloalkyl group, aralkyl group, aryl group or heterocyclic group, A represents an unsubstituted or substituted alkyl group, alkenyl group, cycloalkyl group, aralkyl group, aryl group, heterocyclic group or -NR^{3}R^4 and R^3 and R^4 each independently represents hydrogen, an alkyl group or aryl group and wherein R1 and R2 or R1 and A or R3 and R4 can combine with each other to form a 5- or 6-membered ring.

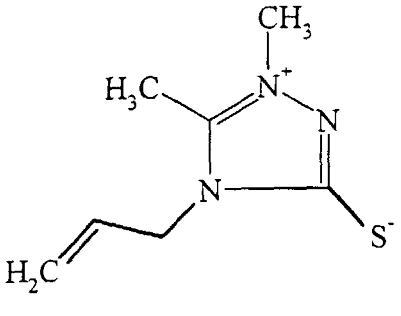
[0022] Specific examples of 1,2,4-triazolium-3-thiolates suitable for use in accordance with the present invention are shown immediately below :



(1)



(2)



(3)

[0023] Preferably the CLA is present in the toner particles for at least 0.5% by weight, more preferably for at least 1% by weight.

[0024] Toner particles having a speed of tribo-electric charging and the stability of the charge for long printing time combined with a narrow charge distribution are very desirable in any printing system using electrostatographic means wherein dry toner particles are used as the marking material.

[0025] Thus, it is preferred in this invention not only to prevent the presence of wrong sign toner and toner with a much too high charge to mass ratio, but also to use toner particles with a charge distribution which is narrow, i.e. the charge of the toner particles shows a distribution wherein the coefficient of variability (ν), i.e. the ratio of the standard deviation to the average value, is equal to or lower than 0.4, preferably lower than 0.3. The charge distribution of the toner particles is measured by an apparatus sold by Dr. R. Epping PES-Laboratorium D-8056 Neufahrn, Germany under the name "q-meter". In United States patents US-A-5 569 567 (Tavernier et al.), US-A-5 622 803 (Tavernier et al.) and US-A-5 532 097 (Tavernier et al.) the preparation of both negatively and positively chargeable toner particles with narrow charge distribution is disclosed. It is a preferred embodiment of the invention to use toner particles prepared according to the method described in these disclosures, that are incorporated herein by reference.

[0026] Thus negatively chargeable toner particles according to this invention further preferably comprise (1) at least one triboelectrically negatively chargeable thermoplastic resin serving as a binder having a volume resistivity of at least 10^{13} Ω-cm, and (2) at least one resistivity lowering substance being an onium compound having a volume resistivity lower than the volume resistivity of the binder, wherein the resistivity lowering substance(s) is (are) capable of lowering the volume resistivity of the binder by a factor of at least 3.3 when present in the binder in a concentration of 5% by weight relative to the weight of the binder. Resistivity decreasing substances suited for use in toner particles according to the present invention are cationic, anionic or amphoteric type surfactants - see e.g. Tensid-Taschenbuch Herausgegeben von Dr. Helmut Stache Carl Hanser Verlag München Wien 1979) or antistatic substances of non-ionic type e.g. non-ionic surfactants or electronically conductive substances. Other useful resistivity decreasing substances (2) are within the following classes of compounds:

- metal salts containing relatively large (bulky) anionic groups;
- betaines;
- amino acids;
- metal complex compounds;
- ionically conductive polymers in which the polymer chain carries anionic groups, e.g. sulphonate groups; and
- electronically conductive polymers, e.g. polyanilines, polypyrroles and polythiophenes.

[0027] Thus positively chargeable toner particles according to this invention further preferably comprise (1) one or more triboelectrically positively chargeable thermoplastic resins serving as a binder having a volume resistivity of at least 10^{13} Ω-cm, and (2) at least one substance having a volume resistivity lower than the volume resistivity of the binder, and wherein the substance(s) (2) when present in the binder in a concentration of 5% by weight lower(s) the volume resistivity of the binder by a factor of at least 3.3. Useful resistivity decreasing substances for use in positively chargeable toner particles of the invention are anionic compounds according to one of following general formulae:

$$(R\text{-}COO)^- M^{n+} \qquad (R\text{-}PO_3)^{2-} M^{2n+}$$

$$(R\text{-}O\text{-}SO_3)^- M^{n+} \qquad (R\text{-}PO_4)^{2-} M^{n+}$$

$$(R\text{-}S\text{-}SO_3)^- M^{n+} \qquad (RH\text{-}PO_4)^- M^{n+}$$

$$(R\text{-}SO_3)^- M^{n+} \qquad (R_2\text{-}PO_4)^- M^{n+}$$

wherein :

R is an organic group, for example:

(1) an unsubstituted or substituted aliphatic, or cycloaliphatic group, e.g. substituted with halogen, aryl, alkoxy or thioether group;
(2) a perfluoroalkyl group, including an aliphatic chain interrupted by one or more hetero atoms, e.g. nitrogen, oxygen or sulphur atom(s), and/or one or more of the hetero atoms being present in one or more substituents on the chain;
(3) substituted or unsubstituted homocyclic aromatic group, including mono- and multi-aromatic ring systems; and
(4) substituted or unsubstituted heterocyclic rings or ring systems.

[0028] Furthermore, M^+ is a cation, e.g. an alkali metal cation, preferably Li^+, and n represents valency number 1 where necessary multiplied by a whole number to satisfy charge equivalency with the negative charge of the associated anionic group.

[0029] Other particularly useful resistivity decreasing substances for use in positively charged toner particles of this invention are nonionic antistatic polyether type compounds, e.g. according to the following general formula :

$$R_1\text{--}[\text{-}O\text{--}(CH_2)_n\text{-}]_m\text{--}R_2$$

wherein each of R_1 and R_2 (same or different) represents hydrogen or an organic group, e.g. an alkyl group, m is a positive integer of at least 20, and n is a positive integer of at least 2.

[0030] The toner particles of this invention are well suited for use in any electrostatographic printing system, and thus the invention encompasses the use of toner particles according to this invention in electrostatographic printing systems, e.g. in electrophotographic printing systems, ionographic printing systems and direct electrostatic printing systems.

[0031] The toner particles of this invention are especially suitable for use in DEP devices, (devices for direct electrostatic printing), wherein electrostatic printing on an image receiving substrate is performed by creating a flow of toner particles from a toner bearing surface to the image receiving substrate and by image-wise modulating the flow of toner particles by means of an electronically addressable printhead structure. In DEP devices wherein charged toner particles are transferred to the surface of a charged toner conveyor, it is observed that the charge to mass ratio of the charged toner particles present upon the charged toner conveyor (CTC) has the tendency to increase as the printing time increases. The reason for this is that not all charged toner particles that pass under the printing apertures are used in the printing so that some of them are carried back to the place where the surface of the CTC is loaded with fresh toner, so that the friction between the toner particles on the surface of the CTC and the fresh toner particles can increase the charge on the toner particles. This is especially so when the surface of the CTC is loaded with charged toner particles from a magnetic brush carrying magnetic carrier particles and non-magnetic toner particles. The reason for this is that the carrier hairs of the magnetic brush further contact the charged toner particles present upon the surface of the charged toner conveyor, increasing their charge to mass ratio, unless they are consumed for image formation and are propelled through the printing apertures. So, if image parts of low or no image density frequently occur in an image, then the charged toner particles are brought in contact with the carrier hairs of the magnetic brush, multiple times before they are consumed, leading to enhanced charge to mass ratio and resulting lowered image density.

[0032] For that reason, it has been described in the literature, to apply the charged toner particles to the charged toner conveyor for just a single revolution of the charged toner conveyor, and to remove all the charged toner particles that have not been used in the printing process before they can contact the carrier hairs of the magnetic brush for a second time. This concept works well, but it requires expensive toner recuperation and recirculation components, and severely limits the choice of charged toner particles to those that are not likely to be destroyed by the recuperation mechanism.

[0033] It has now been found by the inventors that the expensive recuperation means (and resulting partial toner destruction) can be avoided, by using toner particles according to this invention.

[0034] Thus the invention encompasses the use of toner particles according to this invention in a method for direct electrostatic printing comprising the steps of

- providing charged toner particles on an outer sleeve of a charged toner conveyor,
- creating an electric field between the conveyor and an image receiving member, for attracting charged the toner particles to the image receiving member, and
- providing a printhead structure, placed between the conveyor and an image receiving member and having printing apertures coupled to control electrodes coupled to a control voltage, being image-wise modulated for image-wise depositing the charged toner particles on the image receiving member.

[0035] To provide the charged toner particles on the outer sleeve of the charged toner conveyor, a magnetic brush is preferably used carrying magnetic carrier particles and non-magnetic toner particles.

EXAMPLES

The carrier particles

[0036] A macroscopic "soft" ferrite carrier consisting of a MgZn-ferrite with average particle size 50 µm, a magnetisation at saturation of 36 Tm3/kg (29 emu/g) was provided with a 1 µm thick acrylic coating. The material showed virtually no remanence.

The toner particles

Comparative toner (CTI)

[0037] The toner used for the experiment had the following composition : 97 parts of a co-polyester resin of fumaric acid and bispropoxylated bisphenol A, having an acid value of 18 and volume resistivity of 5.1×10^{16} ohm.cm, melt-blended for 30 minutes at 110°C in a laboratory kneader with 3 parts of Cu-phthalocyanine pigment (Colour Index PB 15:3). A resistivity decreasing substance having the formula $(CH_3)_3N^+C_{16}H_{33}$ Br^- was added in a quantity of 0.5% with respect to the binder, as described in International patent specification WO-A-94/027192.

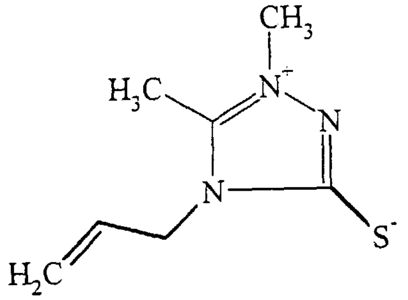
[0038] After cooling, the solidified mass was pulverised and milled using an ALPINE Fliessbettgegenstrahlmühle type 100AFG (trade name) device and further classified using an ALPINE multiplex zig-zag classifier type 100MZR (trade name). The average particle size was measured by Coulter Counter model Multisizer (trade name), and was found to be 6.3 µm by number and 8.2 µm by volume. In order to improve the flowability of the toner mass, the toner particles were mixed with 0.5% of hydrophobia colloidal silica particles (BET-value 130 m^2/g) and hydrophobic colloidal titanium oxide particles.

Comparative toner 2 (CT2)

[0039] The second comparative toner was equal to comparative toner 1 (CT1) except for the addition of 3% by weight of a charge control agent (CCA), COPY CHARGE NCA, (trade name of Clariant) to the bulk of the particles.

Comparative toner 3 (CT3)

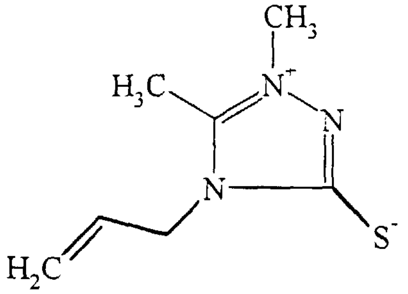
[0040] The third comparative toner was equal to comparative toner 1 (CT1) except for the addition of 2% by weight of a charge limitation agent (CLA), with formula



to the bulk of the toner particles.

Invention toner 1 (IT1)

[0041] The first invention toner was equal to comparative toner 1 (CT1) except for the addition of 2% by weight of a charge control agent (CCA), COPY CHARGE NCA, (trade name of Clariant) and the addition of 0.25% by weight of a charge limitation agent (CLA), with formula



to the bulk of the toner particles.

Invention toner 2 (IT2)

[0042] The second invention toner was equal to the first one except for the addition of 0.5% by weight of the same charge limitation agent (CLA).

Invention toner 3 (IT3)

[0043] The third invention toner was equal to the first one except for the addition of 1% by weight of the same charge limitation agent (CLA).

Invention toner 4 (IT4)

[0044] The fourth invention toner was equal to the first one except for the addition of 2% by weight of the same charge limitation agent (CLA).

Invention toner 5 (ITS)

[0045] The fifth invention toner was equal to the fourth one except for the toner resin, instead of 97 parts of a co-polyester resin of fumaric acid and bispropoxylated bisphenol A, AG23, was used.

Invention toner 6 (IT6)

[0046] The sixth invention toner was equal to the fourth one except for the toner resin, instead of 97 parts of a co-polyester resin of fumaric acid and bispropoxylated bisphenol A, AGII was used.

The developer

[0047] An electrostatographic developer was prepared by mixing the mixture of toner particles and colloidal silica in a 5% ratio (wt/wt) with silicon coated carrier particles.

[0048] The developers were used in a DEP device as described hereinbelow for testing the charging properties of the toner particles.

The printhead structure

[0049] A printhead structure was made from a polyimide film of 50 µm thickness, double sided coated with a 5 µm thick copper film. The printhead structure had two rows of printing apertures. On the back side of the printhead structure, facing the image receiving member, a rectangular shaped control electrode was arranged around each aperture. Each of the control electrodes was connected over 2 MΩ resistors to a HV 507 (trade name) high voltage switching IC, commercially available through Supertex, USA, that was powered from a high voltage power amplifier. The printing apertures were rectangular shaped with dimensions of 360 by 120 µm. The dimension of the central part of the rectangular shaped copper control electrodes was 500 by 260 µm. The apertures were spaced so to obtain a resolution of 33 dots/cm (85 dpi). On the front side of the printhead structure, facing the charged toner conveyer roller, a common shield electrode was arranged around the aperture zone leaving a free polyimide zone of 1620 µm. The printhead structure was fabricated in the following way. First of all the control and shield electrode pattern was etched by conventional copper etching techniques. The apertures were made by a step and repeat focused excimer laser making use of the control electrode patterns as focusing aid. After excimer burning the printhead structure was cleaned by a short isotropic plasma etching cleaning. Finally a thin coating of PLASTIK70, commercially available from Kontakt Chemie, was applied over the control electrode side of the printhead structure.

The charged toner conveyer (CTC)

[0050] The CTC was a cylinder with a sleeve made of aluminium, coated with TEFLON (trade name of Du Pont, Wilmington, USA) with a surface roughness of 0.3 µm (Ra-value) and a diameter of 30 mm.

The printing engine

[0051] Charged toner particles were propelled to this conveyer from a stationary core / rotating sleeve type magnetic brush comprising two mixing rods and one metering roller. One rod was used to transport the developer through the unit, the other one to mix toner with developer.

[0052] The magnetic brush was constituted of the so called magnetic roller, which in this case contained inside the roller assembly a stationary magnetic core, having three magnetic poles with an open position (no magnetic poles present) to enable used developer to fall off from the magnetic roller (open position was one quarter of the perimeter and located at the position opposite to the CTC.

[0053] The sleeve of the magnetic brush had a diameter of 20 mm and was made of stainless steel roughened with a fine grain to assist in transport (Ra=3µm) and showed an external magnetic field strength in the zone between the magnetic brush and the CTC of 0.045 T, measured at the outer surface of the sleeve of the magnetic brush. The magnetic brush was connected to a DC power supply of +140 V. The surface of the charged toner conveyor was positioned at 750 µm from the surface of the magnetic brush, and the surface of the charged toner conveyor was connected to an

AC power supply with a sinusoidally oscillating field of 1800 V (peak to peak) at a frequency of 3.0 kHz with +100 V DC-offset. The surface of the charged toner conveyor was set via PU spacers means at 260 µm from the printhead structure. The shield electrode was connected to a DC power supply (DC5) of +100 V. The control electrodes were connected to a (image-wise selected) DC power source of 0 or +280 V. The back electrode was placed at 1000 µm from the back side of the printhead structure and was connected to a DC power supply of +1250 V. The receiving substrate was moved at a linear speed of 3 m/min, the linear speed of the charged toner conveyor was 6 m/min, and the linear speed of the magnetic brush was 30 m/min.

<u>PRINTING EXAMPLES 1-9</u>

[0054] In these experiments the toner particles as described above (CTI to CT3 and ITI to IT6) were used. After putting a developer comprising 5% of the toner particles in the magnetic brush, the printing engine was started and the charge to mass ratio of the charged toner particles present upon the sleeve of the charged toner M conveyor was measured at different times. The data of these measurements are tabulated in Table 1. Also indicated in Table 1 is a criterion for drop in maximum printing density. An "OK" meant that the maximum density after 1 minute of printing and 1 hour of printing did not differ by more than 10%, when it differed not more than 20% the quotation ACC (acceptable) was given.

Table 1

Measured charge to mass ratio after 30 seconds to 1 hour, and change in maximum printing density between 1 minute and 1 hour.									
Toner used	0.5	1	2′	5′	12′	30′	60′	Q_{05}/Q_{60}	DELTA-D
CT1	9,3	12,0	12,0	na	12,3	20,3	21,4	2.301	NOK
CT2	12,4	13,6	13,7	na	14,3	16,4	17,5	1.411	NOK
CT3	7,9	8,6	9,2	na	9,8	10,6	11,5	1.456	NOK
IT1	12.6	na	na	13.0	na	15.0	19.7	1.563	NOK
IT2	10.9	na	na	12.1	na	13.5	15.2	1.394	ACC
IT3	8.4	na	na	9.8	na	10.0	10.5	1.250	OK
IT4	11,2	10,8	10,9	na	11,3	12,3	11,2	1.000	OK
IT5	11.9	na	na	10.3	na	11.2	11.7	0.983	OK
IT6	9.2	na	na	8.8	na	8.9	10.8	1.174	OK

[0055] From the data in Table 1 it is clear that an acceptable printing reliability regarding maximum printing density can be obtained only when the combination of both a charge controlling agent (CCA) enhancing the charging kinetics, and a charge limiting agent (CLA) limiting the maximum charge to mass ratio, is used. If no CLA is used (as in comparative examples CT1 and CT2) the charge to mass ratio of the charged toner particles present upon the CTC increases to -21 and -17 µC/g (factor 2.301 and 1.411 higher than starting value) resulting in considerably reduced maximum image density. If no CCA is present (as in comparative example CT3) the initial charge to mass ratio at the beginning of the experiment (and every time the toner concentration adjusting mechanism adds new toner particles to the developer) is too low, leading to wrong sign toner, toner accumulation upon the printhead structure and dusting in the magnetic brush. Here the charge to mass ratio levels off at -11.5 µC/g but since the initial value is only -7.9 µC/g a change by a factor of 1.456 is observed between the beginning and end of the printing sequence.

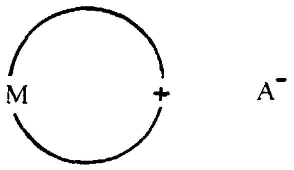
[0056] It is only when at least 0.5% of the CLA is present that the printing results become acceptable and from at least 1% of CLA on the results become good.

Claims

1. Dry toner particles containing a charge control agent (CCA), characterised in that said particles additionally contain a charge limitation agent (CLA).

2. Dry toner particles according to claim 1, wherein said charge limitation agent (CLA) is a meso-ionic compound.

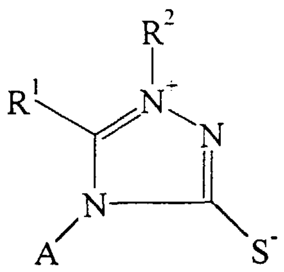
3. Dry toner particles according to claim 2, wherein said meso-ionic compound corresponds to formula (I)



(I)

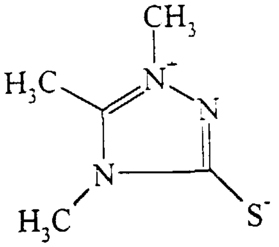
wherein M represents a 5- or 6-membered heterocyclic ring composed of at least one member selected from the group consisting of a carbon atom, an oxygen atom, a sulphur atom and a selenium atom; and A represents -0⁻, -S⁻ or -N⁻-R, wherein R represents an alkyl group, a cycloalkyl group, an alkenyl group, an alkynyl group, an aralkyl group, an aryl group, or a heterocyclic group.

4. Dry toner particles according to claim 2, wherein said meso-ionic compound corresponds to formula correspond to the formula :

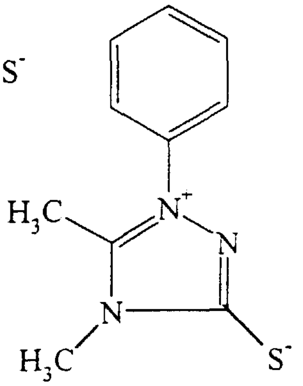


wherein R^1 and R^2 each independently represents an unsubstituted or substituted alkyl group, alkenyl group, cycloalkyl group, aralkyl group, aryl group or heterocyclic group, A represents an unsubstituted or substituted alkyl group, alkenyl group, cycloalkyl group, aralkyl group, aryl group, heterocyclic group or $-NR^3R^4$ and R^3 and R^4 each independently represents hydrogen, an alkyl group or aryl group and wherein R^1 and R^2 or R^1 and A or R^3 and R^4 can combine with each other to form a 5- or 6-membered ring.

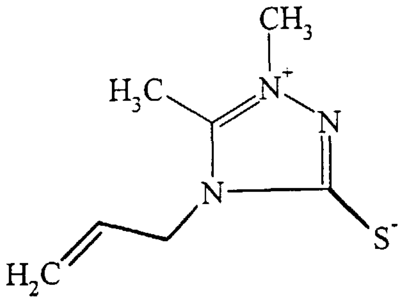
5. Dry toner particles according to claim 2, wherein said meso-ionic compound is a selected from the group consisting of



(1)



(2)



(3)

6. Dry toner particles according to any one of the preceding claims, wherein said CLA is present in at least 0.5% by weight with respect to the total weight of the toner.

7. Use of dry toner particles according any one of the preceding claims in an electrostatographic printing system.

8. Use of toner particles according to any one of claims 1 to 6 in a method for direct electrostatic printing comprising the steps of

- providing charged toner particles on an outer sleeve of a charged toner conveyor,
- creating an electric field between said conveyor and an image receiving member, for attracting charged said toner particles to said image receiving member, and
- providing a printhead structure, placed between said conveyor and an image receiving member and having printing apertures coupled to control electrodes coupled to a control voltage, being image-wise modulated for image-wise depositing said charged toner particles on said image receiving member.

9. Use of toner particles according to claim 8 wherein in said step of providing charged toner particles on an outer sleeve of a charged toner conveyor, a magnetic brush is used carrying magnetic carrier particles and non-magnetic toner particles to provide said charged toner particles on said outer sleeve.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 00 30 8725

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	2 January 2001	Vanhecke, H

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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D : document cited in the application
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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 00 30 8725

02-01-2001

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