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(71) Applicant: AGFA-GEVAERT N.V.
2640 Mortsel (BE)

(72) Inventors:
- Tavernier, Serge
2640 Mortsel (BE)
- Desie, Guido
2640 Mortsel (BE)

(54) A device for direct electrostatic printing (DEP) comprising a toner composition with good conductivity

(57) A DEP device is provided that comprises a toner delivery means (101), a back electrode (105), a printhead structure (106), a final image receiving member (109), a conveyer means (108), a means for fixing (110) said toner onto said final image receiving member, and that is characterised in that said toner delivery means contains toner particles with a specific resistivity of at most 10^9 Ω.cm. It is preferred to use toner particles with a specific resistivity of at most 10^7 Ω.cm. Optionally the DEP device comprises a back electrode that can be heated.

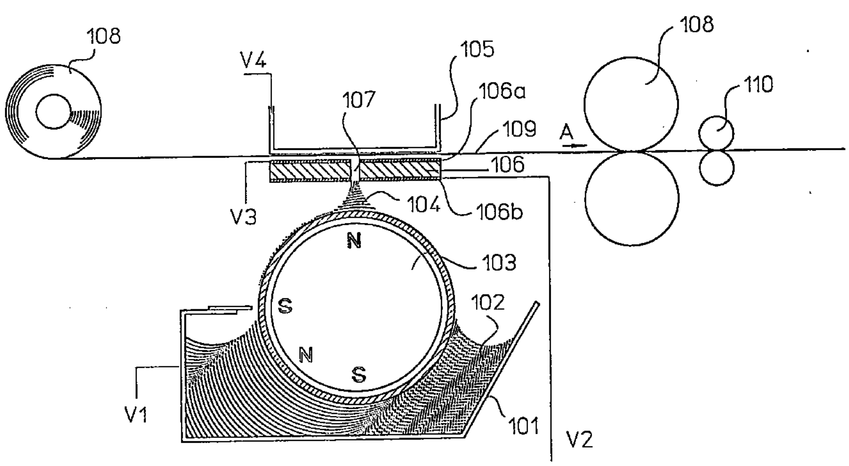

Fig.1

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Description

1. Field of the invention.

This invention relates to method for electrostatic printing and more particularly in Direct Electrostatic Printing (DEP) using a specified type of toner particles. In DEP, electrostatic printing is performed directly from a toner delivery means on a receiving substrate by means of an electronically addressable printhead structure.

2. Background of the Invention.

In DEP (Direct Electrostatic Printing) the toner or developing material is deposited directly in an imagewise way on a receiving substrate, the latter not bearing any latent electrostatic image. In the case that the substrate is an intermediate endless flexible belt (e.g. aluminium, polyimide etc.), the imagewise deposited toner must be transferred onto another final substrate. If, however, the toner is deposited directly on the final receiving substrate, a possibility is fulfilled to create directly the image on the final receiving substrate, e.g. plain paper, transparency, etc. This deposition step is followed by a final fusing step.

This makes the method different from classical electrography, in which a latent electrostatic image on a charge retentive surface is developed by a suitable material to make the latent image visible. Further on, either the powder image is fused directly to said charge retentive surface, which then results in a direct electrographic print, or the powder image is subsequently transferred to the final substrate and then fused to that medium. The latter process results in an indirect electrographic print. The final substrate may be a transparent medium, opaque polymeric film, paper, etc.

DEP is also markedly different from electrophotography in which an additional step and additional member is introduced to create the latent electrostatic image. More specifically, a photoconductor is used and a charging/exposure cycle is necessary.

A DEP device is disclosed in e.g. US-P 3,689,935. This document discloses an electrostatic line printer having a multi-layered particle modulator or printhead structure comprising :

- a layer of insulating material, called isolation layer ;
- a shield electrode consisting of a continuous layer of conductive material on one side of the isolation layer ;
- a plurality of control electrodes formed by a segmented layer of conductive material on the other side of the isolation layer ; and
- at least one row of apertures.

Each control electrode is formed around one aperture and is isolated from each other control electrode.

Selected potentials are applied to each of the control electrodes while a fixed potential is applied to the shield electrode. An overall applied propulsion field between a toner delivery means and a receiving member support projects charged toner particles through a row of apertures of the printhead structure. The intensity of the particle stream is modulated according to the pattern of potentials applied to the control electrodes. The modulated stream of charged particles impinges upon a receiving member substrate, interposed in the modulated particle stream. The receiving member substrate is transported in a direction orthogonal to the printhead structure, to provide a line-by-line scan printing. The shield electrode may face the toner delivery means and the control electrode may face the receiving member substrate. A DC field is applied between the printhead structure and a single back electrode on the receiving member support. This propulsion field is responsible for the attraction of toner to the receiving member substrate that is placed between the printhead structure and the back electrode. Due to the electrical nature of said imaging process, accurate control of the distance of said printhead structure to said toner application module and said image receiving layer is very important, and accurate control of the electrostatic properties of said marking particles irrespective of the environmental conditions is also very important.

In DEP (Direct Electrostatic Printing) a sufficient amount of (free) toner particles has to be present in vicinity of the printing aperture, because when only a low amount of toner particles are present it is only possible to print at low speed and/or with low density. Therefore a cloud of toner particles is provided in the space between the toner supplying member and the printhead structure. Several methods have been proposed to provide such a toner cloud. In, e.g., GB-A 2,108,432 it is disclosed to produce the toner cloud by superimposing an AC (alternating current) field on the direct current (DC) field that is present between the toner supplying member and the printhead. In, e.g., US 4,743,926 it is disclosed to provide a travelling electrical wave on the toner supply member. In EP-A 763 785 it is disclosed to provide a toner cloud either by means of a gas stream or in a fluidized bed. In, e.g., US 5,202,704 mechanical means to provide a toner cloud are disclosed. Whichever means for providing a toner cloud are provided, the incorporation of these means complicates the DEP apparatus.

In any process working according to the principles of electrostatic theory, with electrostatically charged particles, the electrical properties tend to change as a function of changes in the relative humidity of the printing environment. In the electrophotographic apparatus CHROMAPRESS (trade name of Agfa-Gevaert NV, Mortsel, Belgium) both the toner and the final receiving substrate are preconditioned in order to diminish the effect of changes in the relative humidity of the printing environment. In, e.g., US 5,305,026 a device is described comprising an intermediate recording medium upon which the toner image is jetted by using a DEP-process, after which said toner image is transferred to a final receiving member by means of an electrostatic field. The toner image is then fixed on said final receiving member. This apparatus has the advantage that images can be recorded on relatively thick recording media and provided that the electrostatic properties of the intermediate image receiving member is not changed by a changing relative humidity, the problem of changes in image quality due to changes in electrostatic properties of said final receiving member as a result of a changing relative humidity, is excluded. The degrees of freedom in building an apparatus according to the cited disclosure are restricted by the fact that the material used to produce the intermediate toner receiving member must have electrostatic properties that are not changed by a changing relative humidity. Moreover the apparatus becomes complicated and more expensive.

There is still need for improvement DEP devices and methods that do not show the difficulties described above and that are easier to produce.

3. Objects and Summary of the Invention

It is an object of the invention to provide an improved method for Direct Electrostatic Printing (DEP), for printing with high density and high spatial resolution at a final receiving member without significant changes in density and image quality due to a changing relative humidity during printing.

It is a further object of the invention to provide a DEP method combining said possibility of printing with constant density and image quality, with good long term stability and reliability.

Further objects and advantages of the invention will become clear from the description hereinafter.

The above objects are realized by providing a method for direct electrostatic printing (DEP) on an substrate, comprising the steps of :

i) providing an electrical field wherein a flow of charged toner particles is created, from an outer surface of a toner delivery means to said substrate,
ii) image wise modulating said flow of charged toner particles by a printhead structure interposed between said toner delivery means and said substrate and,
iii) image wise depositing said toner particles on said substrate characterised in that said toner particles have a specific resistivity of lower than 10^9 Ω.cm.

4. Brief Description of the Drawings

Fig. 1 is a schematic illustration of a possible embodiment of a DEP device according to the present invention.

5. Detailed Description of the Invention

It is known that conductive toner particles are less sensitive to changes in relative humidity from disclosures on classical electrophotography, e.g., EP-A 618 510 and on stylus based electrographic purposes, e.g., US 3,816,840 and EP-A 661 611.

The possibility of using such toner particles in DEP devices and methods, as described in US 3,689,935, is not obvious. By tying out such particles it was found that the sensitivity of the printing results to changes in relative humidity could be largely diminished and that good printing results could be obtained under various conditions of relative humidity. It was moreover found that said printing results were obtainable at a considerable lower the peak to peak value of the AC-field (alternating current field), than would be expected, superimposed on the DC-field (direct current field), that in many DEP devices is present between the toner supplying member and the printhead structure (see e.g. US 4,491,855). This reduction in peak to peak voltage of the AC-field is beneficial to the longevity of the electronic components use in the DEP device.

When such an AC field is superimposed on the DC-field (direct current field), that in DEP devices is present on the outer surface of the toner supplying member (toner delivery means), the peak to peak voltage of the AC superimposed on said DC-field on said outer surface, will be such that at not any moment the voltage of the AC-field will change the polarity of the DC-field. E.g. when a DC of - 300 V is applied to the outer surface of the toner delivery means, the peak to peak voltage of the superimposed AC field will be at most 600 V.

It was found that said DEP device, gave acceptable printing results once the specific resistivity of the toner particles that were used, was lower than 10^9 Ω.cm. For better printing results, in terms of image density and homogeneity of even density patterns, that were almost insensitive to changing RH (Relative Humidity) (RH ranging from 15 to 85 %), it is preferred that the specific resistivity of the toner particles that are used, is lower than 5.10^7 Ω.cm, more preferably the specific resistivity of the toner particles is lower than 10^7 Ω.cm . In a further preferred embodiment of the method according this invention, using toner particles according to this invention, is implemented in a DEP device having a heated back electrode, made e.g. of stainless steel and incorporating heating means, making it possible to keep the back electrode at a temperature between 120 and 150 °C during printing. The use of a heated back electrode is especially useful when using humidity sensitive substrates to be printed on (e.g. paper, plastic substrate coated with an hydrophilic colloid containing toner receiving layer, etc)).

In a DEP method according to this invention, said electrical field, wherein said flow of charged toner particles is created, may be provided by applying a DC-voltage on said outer surface of said toner delivery means and on a back electrode, so as to provide a potential difference between said outer surface and said back electrode. As mentioned above, when the method according to this invention is implemented in a DEP-device comprising a back electrode, said back electrode comprises preferably heating means.

In a DEP method according to this invention, said substrate can be a non-conductive substrate and can be provided with at least one conductive layer, and said electrical field, wherein said flow of charged toner particles is created, is provided by applying a DC-voltage on said outer surface of said toner delivery means and on said conductive layer, so as to provide a potential difference between said outer surface and said conductive layer on said substrate. Such a method for direct electrostatic printing has been described in European Application 96202228, field on August 8, 1996.

Preparation of the toner particles

As a general approach the preparation of toner particles with low specific resistivity (by low specific resistivity is meant, throughout the whole of this document, a specific resistivity lower than 10^9 Ω.cm) can be done by incorporating an electrically conductive material in the bulk of the toner particles. Although the incorporation of conductive material in the bulk of the toner particles, yields useful toners for use in a DEP device according to the present invention, it is not the most preferred embodiment to provide toners with low specific resistivity for use in this invention. When incorporating a conductive material in the bulk of toner particles, a high concentration of said conductive material is needed, because for the chains in conductivity to extend to the surface of the particles, the conductive particles must almost touch each other thus yielding conductive paths over the resinous matrix of the toner particles. High amounts of additives to the bulk of toner particles can alter the melt-rheological properties of the toner particles by increasing the melt-viscosity of them, unless the properties of the conductive additive and the toner resin are matched such as not to have an interaction between toner resin and additive. This need of no interaction limits the free choice of toner resins and conductive additives. It has been shown in EP-A 628 883 that it was possible to use quite a large amount of inorganic filler in the bulk of toner particles, without influencing the melt-viscosity when the melt viscosity at 120 °C of the toner resin containing 1 m^2 surface of said filler material per gram of resin is, in comparison to the melt viscosity of the same toner resin without said filler material, not raised or at most by a factor f = 1.25. The same test can be applied to the conductive particles that are to be included in the bulk of toner particles useful in this invention.

In a more preferred embodiment, toner particles with low specific resistivity useful in the present invention are produced by providing an electrical conductive layer on top of the toner particles, thus yielding layered toner particles.

It is possible to produce such a conductive layer on top of toner particles in two ways :

1) electrical conductive particles are added to and embedded in the surface of the toner particles and
2) not only conductive particles but also resinous particles are added to the surface of the toner particles in order to build a conductive layer.

In both cases the size of the particles added to the toner particles is small in comparison to that of the toner particles, and should be smaller than 1/10 of the toner-diameter, preferably 1/25 of that diameter. The embedding process and/or layer forming process is in most cases induced by thermal heating above the glass-transition temperature of the toner resin.

A first method for producing a conductive layer on top of toner particles comprises the steps of :

i) adding particles of surface material (conductive particles and optionally resinous particles) as dry powder to toner particles, said toner particles containing a toner resin,
ii) intimately mixing of said surface material with said toner particles, forming a mixture,
iii) heating said mixture under continuous stirring to a temperature above the glass-transition temperature of said toner resin and
iv) cooling said mixture, recovering and classifying said toner particles.

Preferably in step iii) of the method above, the mixture is heated preferentially above the Tg but below the softening temperature of said toner resin and/or layer forming resin.

By this method said conductive particles and optionally resinous particles are embedded in the surface of the toner particle or are fixed as a layer on the toner particles. This layer does not have to be continuous, it was found that depending on the toner resin and the conductive material the desired low specific resistivity could be obtained in with only partially covered toner particles. A second method for producing a conductive layer on top of toner particles comprises the steps of :

i) adding said toner particles to a liquid medium, in which said toner particles are insoluble, forming a dispersion,
ii) adding particles of surface material (conductive particles and optionally resinous particles) to said dispersion,
iii) heating said dispersion under continuous stirring to a temperature above the glass-transition temperature of said toner resin and
iv) cooling said dispersion, recovering and classifying said toner particles.

In step i) of this second method, a co-solvent can be added to said liquid medium, said co-solvent makes it possible to lower the temperature in step iii) of the method by already softening said toner particles at room temperature.

Also by this method said conductive particles and optionally resinous particles are embedded in the surface of the toner particle or are fixed as a layer on the toner particles. This layer does not have to be continuous, it was found that depending on the toner resin and the conductive material the desired low specific resistivity could be obtained in with only partially covered toner particles.

Good electroconductive materials are, e.g. carbon black in the case of black toner, however also colourless electroconductive material is possible such as inorganic particles (SnO_2-based particles, etc) and/or organic conducting materials. The organic materials can be ionic materials (e.g. salts derived from onium-salts) or electron/hole conducting materials (e.g. poly(ethylenedioxythiophene as disclosed in a.o. EP-A 339 340 and EP-A 440 957).

Before use further additives, such as hydrophobic or hydrophillic silica, titania, etc can be added, to the toner particles having a low specific resistivity, useful in this invention, in order to improve other properties such as flow, gloss, etc.

A DEP device, useful, among other implementations of DEP devices, for performing the method according to the present invention, comprises a toner application module, a toner receiving module and a printhead structure which makes it possible to print image density corresponding to an image signal. Said toner application module comprises a container for holding toner particles, a roller structure for providing said toner particles towards said printhead structure and a charge injecting means for charging said toner particles to a certain charge level. Said toner particles are characterised by a sufficient conductivity so that changes in relative humidity have only a minor influence upon the charging characteristics of said toner particles.

A non limitative example of a DEP device according to an embodiment of the present invention is shown in Fig. 1 and comprises :

(i) a toner delivery means (101), comprising a container for toner (102) and a magnetic brush (103) , this magnetic brush forming a mist of charged toner particles (104)
(ii) a printhead structure (106), made from a plastic insulating film, coated on both sides with a metallic film. The printhead structure (106) comprises one continuous electrode surface, hereinafter called "shield electrode" (106b) facing in the shown embodiment the toner delivering means and a complex addressable electrode structure, hereinafter called "control electrode" (106a) around printing apertures (107), facing, in the shown embodiment, the toner-receiving member in said DEP device. Said printing apertures are arranged in an array structure for which the total number of rows can be chosen according to the field of application. The location and/or form of the shield electrode (106b) and the control electrode (106a) can, in other embodiments of a device for a DEP method according to the present invention, be different from the location shown in fig. 1.
(iii) a back electrode structure (105) located behind an image receiving member (109) providing an attractive force for said toner particles towards said image receiving member
(iv) conveyer means (108) to convey said image receiving member (109) over said back electrode structure
(vi) means for fixing (110) said toner onto said final image receiving member, either by contact fusing or by radiation fusing.

Between said printhead structure (106) and the charged toner application module (103) as well as between the control electrode around the apertures (107) and the back electrode (105) located behind the toner receiving member (109) as well as on the single electrode surface or between the plural electrode surfaces of said printhead structure (106) different electrical fields are applied. In the specific embodiment of a device, useful for a DEP method, using a printing device according to the present invention, shown in fig 1. voltage V1 is applied to the sleeve of the magnetic brush 103, voltage V2 to the shield electrode 106b, voltages $V3_0$ up to $V3_n$ for the control electrode (106a). The value of V3 is selected, according to the modulation of the image forming signals, between the values $V3_0$ and $V3_n$, on a time-basis or grey-level basis. Voltage V4 is applied to the back electrode behind the image receiving member 109. In other embodiments of the present invention multiple voltages $V2_0$ to $V2_n$ and/or $V4_0$ to $V4_n$ can be used.

A DEP device according to the present invention, can have also a construction so that the toner is transferred or tackified on an intermediate image receiving member and is transferred to a final substrate by contacting the charged or tackified toner image on said intermediate image receiving member with said final substrate. The toner is then released from said intermediate image receiving member and adheres to the final substrate. This is an indirect electrographic process or a transfusing process. The transfusing can be aided by applying pressure between the intermediate image receiving member and the final substrate, and if necessary a final heat fixing step can still be used. Said intermediate image receiving member in said second embodiment of the present invention must have appropriate thermal characteristics, so that the temperature can be rapidly increased and reproducibly from said zone of toner application to said zone of toner transfusing so that the jumped toner image is not distorted too much after the final transfusing to said final image receiving member. Therefore, said intermediate image bearing member is characterized by a compromise between heat capacity, thermal conductivity, thickness and speed. Said compromise can very well be reached by using an intermediate image bearing member in belt form and by constructing said belt with a polymeric film that carries vacuum deposited aluminum (thickness of the aluminum layer between 100 and 2000 nm) and that has a surface coated with poly(tetrafluoroethylene). The temperature on the toner side of such a belt is enhanced by an heating source and ideally is brought to a low temperature again at the back electrode (105) position. Said heating source can be any known heating source, e.g. a radiation source or a contact heating source. If the heating by said heating source is not sufficient, also said transfer means can be heated or the intermediate image bearing member can carry an additional internal heating source. It is possible to construct an intermediate image receiving member according to the present invention as a non-cylindrical belt as described in e.g. US 5,103,263. Although the heating of said intermediate image receiving member, in said second embodiment of the present invention is preferentially carried out by irradiation heating from the toner side and by a radiative power source located outside of said intermediate image receiving member, said heating can also be caused by contact pressure or by irradiative heating from the back-side of said tuner image.

In figure 1 a magnetic brush with magnetic mono-component toner particles is used as toner application module. Charged toner particles are extracted directly from said magnetic brush. In other embodiments of the present invention charged non-magnetic monocomponent conductive toner particles can be applied to the surface of a roller structure, from which they can be extracted and propelled towards said printhead structure. The toner particles with low specific resistivity, according to the present invention, can be used as a mono-component magnetic developer and as a mono-component non-magnetic developer. The toner particles according to the present invention can also be used in a DEP device functioning with a multi-component developer or can be used as non-magnetic mono-component developer.

The toner particles used in a DEP method according to the present invention can essentially be of any nature as well with respect to their composition, shape, size, and preparation method and sign of their tribo-electrically acquired charge, as long as the conductivity of the toner particles is within the range disclosed in this invention. Typical examples of useful toner particles can be found in e.g. US 5,457,001, US 3,639,245, EP-A 441 426 and EP-A 280 789.

Said printhead structure is positioned between said toner application module and said toner receiving member. In a specific embodiment of the present invention said printhead structure is made of a plastic nonconducting material through which individual apertures are made and control electrodes positioned around said apertures are able to modify the flux of charged toner particles through said apertures. In other embodiments of this invention said printhead structure can also comprise a second conduction layer at the other surface side of said printhead structure, so that a three-layered structure is obtained : i.e. a conducting electrode layer, a non-conducting isolation layer and a second conducting electrode layer. Some or all conducting electrode layers in a DEP device according to the present invention can optionally be coated with a thin protective dielectric layer. The apertures in these printhead structures can have a constant diameter, or can have a broader entrance or exit diameter. Other possibilities of printhead structures usable in the present invention include a woven canvas structure and a hybrid structure with an isolating substrate and control electrodes on one side and a wire structure on the other side.

The back electrode (105) of a DEP device, according to the present invention, can also be made to cooperate with the printhead structure, said back electrode being constructed from different styli or wires that are galvanically isolated and connected to a voltage source as disclosed in e.g. US-P 4,568,955 and US-P 4,733,256. The back electrode, cooperating with the printhead structure, can also comprise one or more flexible PCB's (Printed Circuit Board).

When a back electrode is used the electrical field wherein a flow of charged toner particles from said toner delivery means to said substrate is created, according to the method according to this invention, is a potential difference between the toner delivery means and the back electrode, and as shown in figure 1, the receiving substrate is passed between the printhead structure and the back electrode. Mostly this electrical field is a DC-field, whereon, if so desired, a AC field can be superimposed.

The electric field, wherein a flow of charged toner particles from said toner delivery means to said substrate is created, can, in a method according to this invention, be applied between said toner delivery means and a conductive layer present on the face of the receiving substrate facing the toner delivery means. Such a method for direct electrostatic printing has been described in European Application 96202228, field on August 8, 1996.

When a magnetic brush is used as toner source in a DEP device according to this invention, said magnetic brush

103 is preferably of the type with stationary core and rotating sleeve.

A DEP device making use of the above mentioned marking toner particles can be addressed in a way that enables it to give black and white. It can thus be operated in a "binary way", useful for black and white text and graphics and useful for classical bi-level half-toning to render continuous tone images.

A DEP device according to the present invention is especially suited for rendering an image with a plurality of grey levels. Grey level printing can be controlled by either an amplitude modulation of the voltage V3 applied on the control electrode 106a. In a preferred embodiment of this invention, the grey-level printing is performed by a time modulation of V3. By changing the duty cycle of the time modulation at a specific frequency, it is possible to print accurately fine differences in grey levels. It is also possible to control the grey level printing by a combination of an amplitude modulation and a time modulation of the voltage V3, applied on the control electrode.

The combination of a high spatial resolution and of the multiple grey level capabilities typical for DEP, opens the way for multilevel half-toning techniques, such as e.g. described in the EP-A 634 862. This enables the DEP device, according to the present invention, to render high quality images.

A DEP device according to the present invention can be incorporated in monochrome printers or in colour printers. Said printers can incorporate one or more DEP device according to this invention. Especially when used in colour printers it is useful to use at least two DEP devices according to the present invention.

DEP devices according to this invention can also be combined with classical electro(photo)graphic devices to form a printer.

EXAMPLES

Preparation of the toner particles

TONER T1

i) Preparation of the toner core

A toner was prepared by melthomogenisation of 45 parts by weight (45 % wt/wt) of a linear polyester of propoxylated bisphenol A and fumaric acid, commercially available as ATLAC T500 (ATLAC is a registered trade name of Atlas Chemical Industries Inc. Wilmington, Del. U.S.A.) with magnetic oxide (magnetite) (45 % wt/wt) EPT1000 (trade name of Nordmann Company, Hamburg, Germany. This magnetite was cubic, had an oil absorption surface of 21 m^2/100 g, a saturation magnetization of 0.104 mT.m^3/kg (83 emu/g) and a coercivity of 1.5 10^4 A/m (190 Oe). The melthomogenisation was done in a melt homogenisation kneader for 30 minutes at 120 °C. Afterwards the mixture was cooled down and milled with an Alpine Fliessbeth-Gegenstrahlmühle (A.G.F.) type 100 as milling means and the Alpine Multiplex Zick-Zack Sichter as air classification means, available from Alpine Process Technology, Ltd., Rivington Road, Whitehouse, Industrial Estate, Runcorn, Cheshire, UK.
The particle size distribution had a $d_{n,50}$ (numerical average diameter) of 10.4 μm and a $d_{v,50}$ (volume average diameter) of 14 μm, when measured with a COULTER COUNTER (registered trade mark) Model TA II particle size analyzer operating according to the principles of electrolyte displacement in narrow aperture and marketed by COULTER ELECTRONICS Corp. Northwell Drive, Luton, Bedfordshire, LC 33, UK.

ii) Surface treatment of the toner core

To said toner core particles 5 % wt/wt of carbon black (CABOT REGAL 400, trade name of Cabot Corp. High Street 125, Boston, U.S.A.) was added. The mixture was homogenised in a dry state using an Henschel mixer. The resulting material was fed into the jet of a hot air spraying device operated with an air temperature of 220 °C, cooled down by admixing cold air and recovered from the air stream by a cyclone. After this process 1 % wt/wt of hydrophobic SiO_2 was added (AEROSIL R972, tradename of Degussa, Germany) and the spraying process was repeated at 250 °C in order to fuse intimately the surface material to the toner surface. Then the mixture was again cooled down by admixing cold air and the toner particles recovered from the air stream by a cyclone.

TONER T2

i) Preparation of the toner core

The preparation of toner core particles was equal to the one described in preparation of toner T1.

ii) Surface treatment of the toners

To said toner core 5 % wt/wt of carbon black (CABOT REGAL 400, trade name of Cabot Corp. High Street 125, Boston, U.S.A.) was added. The mixture was homogenised in a dry state using an Henschel mixer. The resulting mixture was dispersed into water with 10 % by weight (5 % wt/wt) ethanol as co-solvent and 1 % wt/wt of polyoxyethylene wetting agent. The dispersion was found to be stable and was heated up to 55 °C, upon which embedding of the carbon proceeded. After 15 minutes of treatment, the dispersion was allowed to cool and the material recovered and dried. After drying, 1 % wt/wt of hydrophobic SiO_2 was done (AEROSIL R972, tradename of Degussa, Germany) was added in order.

TONER T3

The preparation of toner T1 was repeated except for the amount of carbon black that was embedded in the surface of the toner. In stead of 5 % wt/wt of carbon black (CABOT REGAL 400, trade name of Cabot Corp. High Street 125, Boston, U.S.A.) only 2.5 % wt/wt was used.

TONER T4

The preparation of toner T1 was repeated except for the type of carbon black that was embedded in the surface of the toner. In stead of 5 % wt/wt of carbon black CABOT REGAL 400, (trade name of Cabot Corp. High Street 125, Boston, U.S.A.), 5 % of carbon black VULCAN XC-72 R (trade name of Cabot Corp. High Street 125, Boston, U.S.A.) was used.

TONER T5

The preparation of toner T4 was repeated except for the amount of carbon black that was embedded in the surface of the toner. In stead of 5 % wt/wt of carbon black (VULCAN XC-72 R trade name of Cabot Corp. High Street 125, Boston, U.S.A.), 2.5 % of wt/wt of carbon black (VULCAN XC-72 R trade name of Cabot Corp. High Street 125, Boston, U.S.A.), was used.

Measurement of Specific resistivity

The specific resistivity of the material was determined by tapping toner-particles in a measuring cell with a surface of 10^2 cm^2 and a gap of 0.5 cm. The specific resistivity was measured by measuring the current upon applying a voltage of 1000 V direct current (DC) and reading the current after allowing 30 seconds for equilibration. Resulting values are listed in table 1.

Measurement of printing quality

A printout was made with a DEP device and various toner particles as described above at an environmental relative humidity of 15, 50 and 85%, and the image was judged for image density and image quality (homogeneity of the image). For each of the image quality parameters cited above the level was expressed in plus and minus signs as follows :

++ : very good
+ : good
0 : moderate
- : bad
-- : unacceptable

The results are given in table 1.

EXAMPLE 1 (E1)

The printhead structure (106)

A printhead structure 106 was made from a polyimide film of 75 µm thickness, double sided coated with a 7 µm thick copper film. On the back side of the printhead structure, facing the receiving substrate, a square shaped control electrode 106a was arranged around each aperture. Each of said control electrodes was individually addressable from a high voltage power supply. On the front side of the printhead structure, facing the toner delivery means, a common shield electrode (106b) was present. The printhead structure 106 had four rows of apertures. The apertures were square shaped and had an width of 125 μm. The width of the scare shaped copper control electrodes was 225 μm. The rows of apertures were staggered to obtain an overall resolution of 200 dpi (dots per inch) or 80 dots per cm.

For the fabrication process of the printhead structure, conventional methods of copper etching ad plasma etching were used, as known to those skilled in the art.

The toner delivery means (101)

The toner delivery means 101 comprised a stationary core/rotating sleeve type magnetic brush (103) comprising two mixing rods and one metering roller. One rod was used to transport the toner through the unit, the other one to mix the toner particles.

The magnetic brush 103 was constituted of the so called magnetic roller, which in this case contained inside the roller assembly a stationary magnetic core, having nine magnetic poles with an open position (no magnetic poles present).

The sleeve of said magnetic brush had a diameter of 60 mm and was made of stainless steel roughened with a fine grain to assist in transport (Ra=3 μm) and showed an external magnetic field strength in the zone between said magnetic brush and said printhead structure of 0.045 T, measured at the outer surface of the sleeve of the magnetic brush.

A scraper blade was used to force toner to leave the magnetic roller. On the other side a doctoring blade was used to meter a small amount of toner onto the surface of said magnetic brush.

The sleeve was rotating at 100 rpm, the internal elements rotating at such a speed as to conform to a good internal transport within the development unit. The magnetic brush 103 was connected to an high voltage power supply of -300 V.

The printing engine

The distance between the front side of the printhead structure 106 and the sleeve (reference surface) of the magnetic brush 103, was set at 400 μm. The distance between the back electrode 105 of the image receiving member 109 and the back side of the printhead structure 106 (i.e. control electrodes 106a) was set to 700 μm and sad image receiving member travelled at 1 cm/sec. The shield electrode 106b was connected to the -300 V high voltage power supply. To the individual control electrodes an (imagewise) voltage V3 between 0 V and -300 V was applied. The back electrode 105 was made of stainless steel with heating elements in the back electrode and connected to a high voltage power supply of +1300 V. During printing the back electrode was held at a temperature between 120 and 130 °C. To the sleeve of the magnetic brush a voltage of -300 V was applied. The printing proceeded by using toner T1.

EXAMPLE 2 (E2)

In example 2 a print was made with the same configuration as described in example 1, but with toner T2.

COMPARATIVE EXAMPLE 1 (CE1)

In comparative example 1 the same configuration as described in example 1 was used, but with toner T3.

COMPARATIVE EXAMPLE 2A (CE2A)

The printing configuration of example 1 was used except for the fact that the magnetic brush carried a multi-component developer comprising a ferrite carrier with average volume diameter 50 μm and 4 % by weight of toner particles. The toner particles were prepared by melt kneading 97 parts of a copolyester resin of fumaric acid and propoxylated bisphenol A, having an acid value of 18 and volume resistivity of 5.1 x 10^{16} ohm.cm 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 following 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 WO 94/027192. The toner particles had a specific resistance of 1 10^{14} Ω.cm. After cooling, the solidified mass was pulverized and milled using an ALPINE Fliessbettgegenstrahlmühle type 100AFG (tradename) and further classified using an ALPINE multiplex zig-zag classifier type 100MZR (tradename). The average particle size was measured by Coulter Counter model Multisizer (tradename), 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 hydrophobic colloidal silica particles (BET-value 130 m^2/g).

The sleeve of the magnetic brush (V1 in figure 1) was connected to an AC power supply with a square wave oscillating field of 600 in 3.0 kHz with 0 V DC-offset and the shield electrode was grounded.

COMPARATIVE EXAMPLE 2B (CE2B)

Comparative example 2A was repeated, except that no AC-voltage was applied to the sleeve of the magnetic brush.

EXAMPLE 3 (E3)

In example 3 the same configuration as described in example 1 was used, but toner T4 was used.

EXAMPLE 4 (E4)

In example 4 the same configuration as described in example 1 was used, but toner T5 was used.

TABLE 1

Ex nr	Resitivity Ω.cm	Image density			Image homogeneity		
		15*	50*	85*	15*	50*	85*
E1	$1.6\ 10^{7}$	+	+	+	+	+	++
E2	$9.9\ 10^{6}$	++	++	+	++	++	+
CE1	$1.6\ 10^{9}$	--	--	--	n**	n	n
CE2A	$1.0\ 10^{14}$	--	++	-	n	+	0
CE2B	$1.0\ 10^{14}$	--	--	--	n	n	n
E3	$4.0\ 10^{6}$	++	++	++	++	++	++
E4	$3.8\ 10^{7}$	0	0	0	+	+	++

* = % Relative humidity at printing
** n = could not be judged, too low density

Claims

1. A method for direct electrostatic printing (DEP) on an substrate, comprising the steps of :

i) providing an electrical field wherein a flow of charged toner particles is created, from an outer surface of a toner delivery means to said substrate,
ii) image wise modulating said flow of charged toner particles by a printhead structure interposed between said toner delivery means and said substrate and,
iii) image wise depositing said toner particles on said substrate characterised in that said toner particles have a specific resistivity of lower than 10^9 Ω.cm.

2. A method according to claim 1, wherein said specific resistivity of said toner particles is smaller than $5\ 10^7$ Ω .cm.

3. A method according to claim 1, wherein said specific resitivity of said toner particles is smaller than $1\ 10^7$ Ω .cm.

4. A method according to any of the preceding claims, wherein said electrical field, wherein said flow of charged toner particles is created, is provided by applying a DC-voltage on said outer surface of said toner delivery means and on a back electrode.

5. A method according to claim 4, wherein said back electrode comprises heating means.

6. A method according to any of claims 1 to 3, wherein said substrate is provided with at least one conductive layer, and said electrical field, wherein said flow of charged toner particles is created, is provided by applying a DC-voltage on said outer surface of said toner delivery means and on said conductive layer.

7. A method according to any of the preceding claims, wherein an AC-voltage is superimposed on said DC-voltage present on said outer surface of said toner delivery means.

8. A DEP device according to claim 7, wherein said AC-voltage has a peak to peak voltage such that said AC-voltage does not change the polarity of said DC-field.

9. A method according to any one of the preceding claims, wherein said toner particles have been prepared by a method comprising the steps of :

   i) adding particles of surface material (conductive particles and optionally resinous particles) as dry powder to toner particles, said toner particles containing a toner resin,
   ii) intimately mixing of said surface material with said toner particles, forming a mixture,
   iii) heating said mixture under continuous stirring to a temperature above the glass-transition temperature of said toner resin and
   iv) cooling said mixture, recovering and classifying said toner particles.

10. A method according to claim 9, wherein said mixture was heated to a temperature above the glass-transition temperature and below the softening temperature of said toner resin.

11. A method according to any one of claims 1 to 8, wherein said toner particles have been prepared by a method comprising the steps of :

   i) adding said toner particles to a liquid medium, in which said toner particles are insoluble, forming a dispersion,
   ii) adding particles of surface material (conductive particles and optionally resinous particles) to said dispersion,
   iii) heating said dispersion under continuous stirring to a temperature above the glass-transition temperature of said toner resin and
   iv) cooling said dispersion, recovering and classifying said toner particles.

12. A method according to claim 11, wherein a co-solvent is added to said liquid medium.

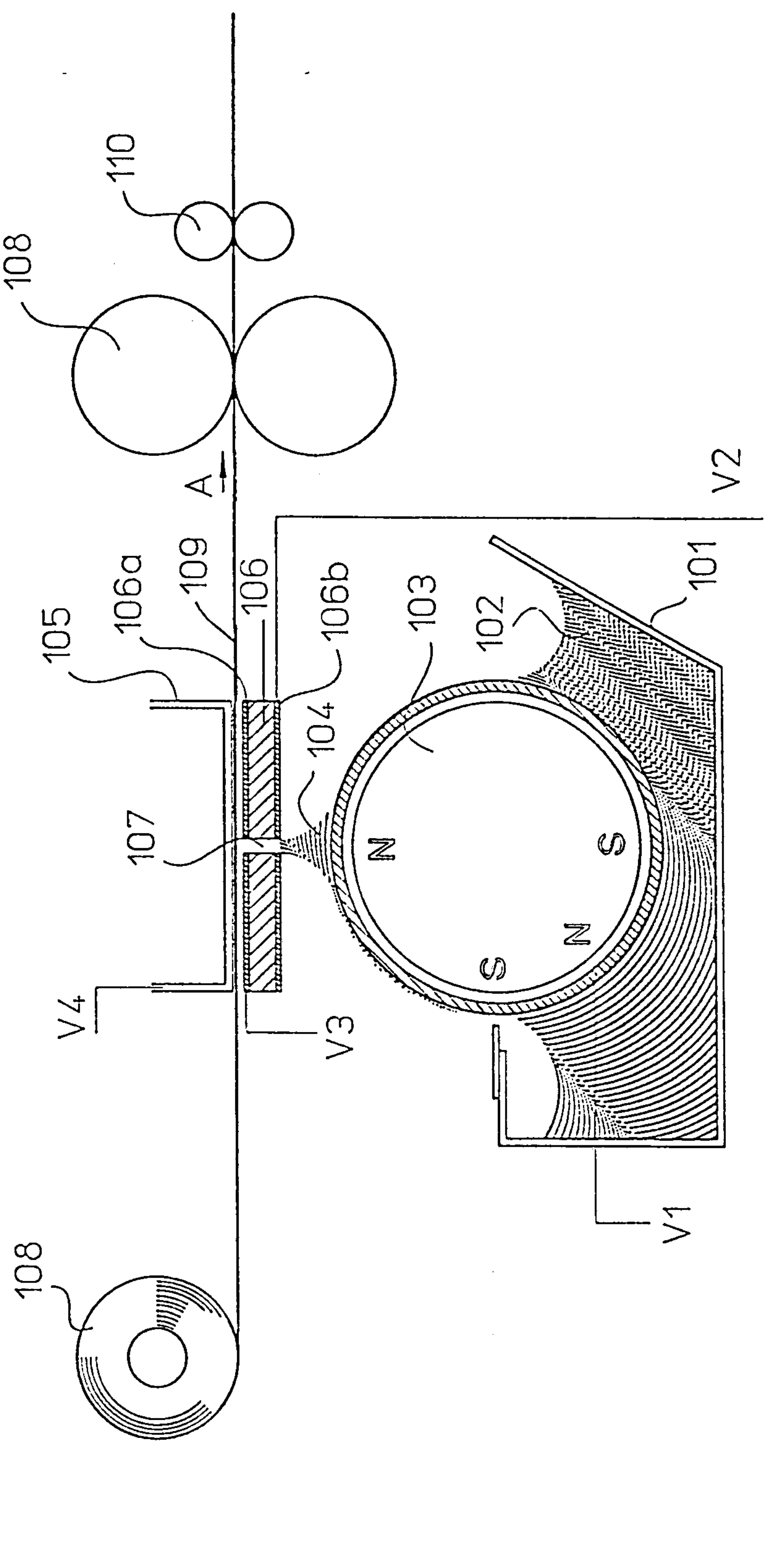
108
110
A
V2
101
102
103
106b
106
109
106a
105
104
107
N
S
N
S
V4
V3
V1
108

Fig.1