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(54) A method for direct electrostatic printing using toner particles with adapted charging properties

(57) A method for direct electrostatic printing wherein charged toner particles are brought on the surface of a charged toner conveyor from where they are attracted to an image receiving substrate and wherein the toner particles have adapted charging properties so that the initial charge of them is after printing 1 hour changed by no more than a factor 1.400. The toner particles comprise a charge control agent and a charge limitation agent, the latter preferably being a meso-ionic compound.

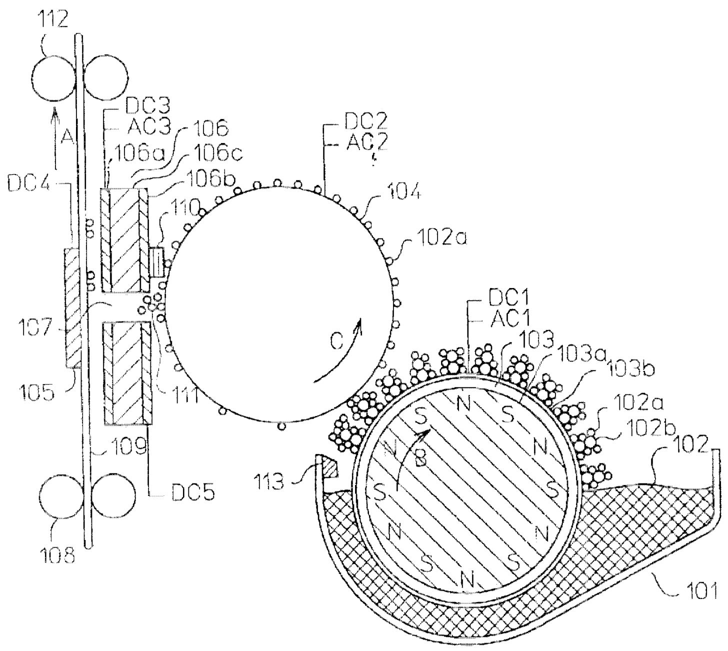

Fig. 1

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Description

FIELD OF THE INVENTION

[0001] This invention relates to a recording method and an apparatus for use in the process of Direct Electrostatic Printing (DEP), in which an image is created upon a receiving substrate by creating a flow of 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.

BACKGROUND OF THE INVENTION

[0002] In DEP (Direct Electrostatic Printing) toner particles are deposited directly in an image-wise way on a receiving substrate, the latter not bearing any image-wise latent electrostatic image.

[0003] 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, or from electrophotography in which an additional step and additional member is introduced to create the latent electrostatic image (photoconductor and charging/exposure cycle).

[0004] A DEP device is disclosed in e.g. **US-A-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.

[0005] Each control electrode is formed around one aperture and is isolated from each other control electrode.

[0006] Selected electric 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 support for a toner receiving substrate 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 substrate, interposed in the modulated particle stream. The receiving substrate is transported in a direction perpendicular to the printhead structure, to provide a line-by-line scan printing. The shield electrode may face the toner delivery means and the control electrodes may face the receiving substrate. A DC-field is applied between the printhead structure and a single back electrode on the receiving substrate. This propulsion field is responsible for the attraction of toner to the receiving substrate that is placed between the printhead structure and the back electrode.

[0007] One of the problems with this type of printing devices is that charged toner particles can accumulate upon the printhead structure and in the printing apertures. Due to this problem the achievable printing density does not remain constant in the time, while the charged toner particles accumulated on the printhead structure may change the electrical field wherein the charged toner particles are propelled towards the substrate and the toner particles accumulated in the printing apertures can physically block the toner passage.

[0008] Several disclosures concerning devices that can clean up a printhead structure after it has been smudged with toner particles are known in the art.

[0009] In other disclosures, ways and means are disclosed to prevent the smudging of the printhead structure in the first place. In, e.g., **US-A-4 755 837** and **US-A-4 814 796** it is disclosed that the presence of Wrong Sign Toner (WST) is the main cause of accumulation of toner particles upon said printhead structure and in the printing apertures. Wrong sign toner particles are particles that have a sign different from that of the majority of the particles. Therefore they respond to the applied electrical fields for creating a flow of charged toner particles to the substrate in an opposite way than the majority of the toner particles. In these disclosures it has been described that the problem of wrong signed toner can be solved when in a device for direct electrostatic printing the flow of toner particles towards the substrate originates from the surface of a conveyer for charged toner particles (hereinafter indicated as "charged toner conveyer" or CTC) whereon well behaved (i.e. wherein no wrong sign toner is present) charged toner particles are deposited by using a magnetic brush comprising two-component developer.

[0010] An other way to avoid the presence of wrong signed toner is to use a magnetic brush with two-component developer in which the toner particles are charged to a high charge-to-mass ratio (μC/g) for bringing charged toner particles to the surface of the CTC. However, a high charge-to-mass ratio leads to a high sticking force of charged particles to electrode surfaces of opposite polarity so that printing at high speed with sufficient density becomes problematic. It is, e.g. indicated in **EP-A-811 894** that a higher charge-to-mass ratio can also lead to an unevenness in image parts of maximum and moderate density.

[0011] In **US-A-5 337 124** and **EP-A-740 224** a toner application module for electrophotographic and electrographic printing has been described in which two different magnetic brushes are used, one to supply toner particles to a charged toner conveying roller and one recuperate them from said roller. This is a system wherein a pushing magnetic brush brings the toner particles to the surface of the CTC and after the surface of the CTC has passed near the printing apertures a pulling magnetic brush is used to clean the surface of the CTC.

[0012] In **European application 98202607**, filed on August 3, 1998, **European Application 98203008**, filed on September 8, 1998 and **European Application 98203873**, filed on November 16, 1998 a toner application module has been described in which a single magnetic brush and a cleaning blade are used, said one magnetic brush to supply toner particles to a charged toner conveying roller and said cleaning blade to recuperate them from said roller. This is a system wherein the magnetic brush brings the toner particles to the surface of the CTC and after the surface of the CTC has passed near the printing apertures a cleaning blade is used to clean the surface of the CTC. In this configuration charged toner particles are only applied once to the surface of said charged toner conveyor, and as a result the charge to mass ratio of the charged toner particles can't be enhanced by multiple contacts with carrier hairs touching said charged toner particles multiple times before they are propelled through said printhead apertures. Since the charge to mass ratio is not increasing as a function of printing time, the resulting printing density is not decreasing as a function of printing time. However, said charged toner particles may not be damaged by the recuperation process and have to be recycled, making the system complex and expensive.

[0013] In all of these prior art applicator designs, the long term stability of the charge-to-mass ratio during the complete printing process is not easily achieved in an economical way. Thus there is still a need for less expensive DEEP devices making it possible to print at elevated speed with no or very low toner accumulation upon said printhead structure and with a reliable and constant flow of well behaved charged toner particles from said toner application module.

OBJECTS AND SUMMARY OF THE INVENTION

[0014] It is an object of the invention to provide a DEP device, i.e. a device for direct electrostatic printing, that can print at high speed with low clogging of the printing apertures and with high and constant maximum density over a long period of time.

[0015] A further object of the invention is to provide an inexpensive DEP device that can print at high speed with low clogging of the printing apertures and with high and constant maximum density over a long period of time.

[0016] Further objects and advantages of the invention will become clear from the detailed description herein after.

[0017] The object of the invention is realised by providing a method for Direct Electrostatic Printing (DEP) comprising the steps of :

- providing charged toner particles having an average charge to mass ratio Q1/m on an outer sleeve of a charged toner conveyor,
- adapting said toner particles so that after 30 seconds of printing said average charge to mass reaches a value of Q2/m, said value after 1 hour of printing changing by a factor of not more than 1.400,
- creating an electric field between said conveyor and an image receiving member, for attracting charged said toner particles to said image receiving member, and
- 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.

[0018] In a preferred embodiment, in said step of adapting said toner particles both a charge control agent (CCA) and a charge limitation agent (CLA) are incorporated in said toner particles.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019] Figure 1 shows schematically a DEP device according to the present invention using toner particles comprising a charge control agent (CCA) and a charge limitation agent (CLA) in a magnetic brush applying said charged toner particles to a charged toner conveyor.

DETAILED DESCRIPTION OF THE INVENTION

[0020] It is known in the art of DEP (direct electrostatic printing), that toner accumulation on the printhead structure and in the printing apertures can partially or completely block said printing apertures, leading to white stripes of missing dots. Adherence of toner particles can be avoided by using charged toner particles having a high charge to mass ratio and a low population of wrong sign toner (WST), i.e. toner particles having a polarity that is opposite to the polarity of most of the charged toner particles.

[0021] However, it is known in the literature, that choosing toner particles with a high charge to mass ratio, lead to lowering the image density. Moreover, when in a DEP device charged toner particles are transferred to the surface of a charged toner conveyor, then 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 do further contact the charged toner particles present upon the surface of the charged toner conveyor, increasing there charge to mass ratio, unless the are consumed for image formation and are propelled through said printing apertures. So, if image parts of low or no image density frequently occur in an image, then said charged toner particles are brought in contact with the carrier hairs of said magnetic brush, multiple times before they are consumed, leading to enhanced charge to mass ratio and resulting lowered image density.

[0022] For that reason, it has been described in the literature, to apply said charged toner particles to said charged toner conveyor for just a single revolution of said charged toner conveyor, and removing 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 perfectly well, but it requires expensive toner recuperation and recirculation components, and is very limiting towards the charged toner particles that may not be destroyed by the recuperation mechanism.

[0023] It has been found that said expensive recuperation means (and resulting partially toner destruction) can be avoided, by using a toner that is adapted in charging kinetics and charging limits, so that after 30 seconds of printing the average charge to mass reaches a value of Q2/m, said value after 1 hour of printing changing by a factor of not more than 1.400. Preferably said value changes by a factor of not more than 1.300

[0024] The use of such toner particles is beneficial in any DEP device wherein charged toner particles are loaded on a CTC from a toner source. Thus DEP devices wherein charged toner particles are loaded on a CTC via a toner dispensing part of a non-magnetic development system held at a distance of the CTC, wherein charged toner particles are loaded on a CTC via a toner dispensing part of a non-magnetic development system held in contact with the CTC, and devices wherein charged toner particles are loaded on a CTC via a magnetic brush containing magnetic carrier particles and non-magnetic carrier particles can all beneficially be operated in a method according to this invention using toner particles with adapted charging properties. It is especially beneficial to operate DEP devices, wherein charged toner particles are loaded on a CTC via a magnetic brush containing magnetic carrier particles and non-magnetic carrier particles, in a method according to this invention using toner particles with adapted charging properties.

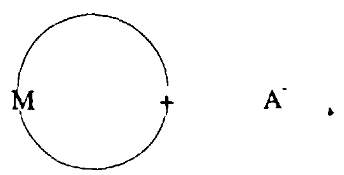
[0025] Said toner particles are adapted via incorporation of charge control agents (CCA) to obtain very fast charging kinetics, while their charge to mass ratio is limited to a certain value by incorporation of charge limitation agents (CLA). The combination of charge control agents (CCA) and charge limitation agents (CLA) provide very useful properties: i. e. the toner particles are charged very rapidly to a minimum charge to mass ratio, and after transfer of said toner particles to the charged toner conveyor a layer of charged toner particles is provided with sufficient charge to mass ratio, so as to prevent toner adhesion to said printhead structure as a result of wrong sign toner or toner with a much too small charge to mass ratio. On the other hand, if in an image no or very low toner consumption is required, then said charged toner particles remain on the surface of said charged toner conveyor for a long time during which multiple new contacts with fresh toner particles and/or with carrier particles of the carrier hairs in the magnetic brush take place, but due to the charge limiting agents incorporated in said toner particles, the resulting charge to mass ratio of said toner particles upon said charged toner conveyor do not exceed the threshold value. As a result, even without toner recuperation and recycling unit, constant charge to mass ratio of charged toner particles upon said charged toner conveyor is obtained, resulting in image densities which remain constant in time and do not drop as a function of printing time as in the prior art description which do not utilise an expensive toner recuperation and recycling unit.

[0026] The toner particles with adapted charging properties for use in the method of this invention can further incorporate any ingredient known in the art, e.g., toner resin, a colorant, metal oxides, etc.. The toner particles with adapted charging properties for use in the method of this invention can be toner particles with a negative charge as well as toner particles with a positive charge. When toner particles with 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, for toner particles with positive charge, mainly ammonium compounds, pyridinium compounds, triphenylmethane, cationic dyes, negrosine dyes, etc. are used. for toner particles with positive charge, mainly metal complexes, phenylsilicates, naphthylsilicates, azo compounds, cationic polymers, modified ammonium compounds etc. are used. Charge control agents for positive charging are commercially available through e.g. Ciba-Geigy of Switserland 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, etc. 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, etc.

[0027] The charge limitation agent (CLA) used for adapting the charging properties of toner particles used in the method of this invention are meso-ionic compounds.

[0028] 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. 11, p. 15 (1957) and Advances in Heterocyclic Chemistry, Vol. 19, P. 4 (1976).

[0029] Preferred meso-ionic compounds are those represented by formula (I):

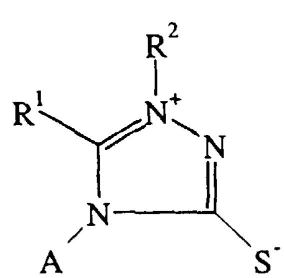


formula (I)

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).

[0030] 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. Meso-ionic compounds are known for use in the fixing step of a photographic process as disclosed in EP-A-431 568. Triazolium thiolate meso-ionic compounds are well known in silver halide photography and are used e.g. for increasing temperature latitude as disclosed in JP-A-60-117240, for reducing fog as disclosed in US-A-4 615 970, in preparing silver halide emulsions as disclosed in US-A-4 631 253, in bleach etching baths as disclosed in EP-A-321 839, to prevent pressure marks as disclosed in US-A-4 624 913, in EP-A-554 585 for enhancing the printing properties and especially the printing endurance of a lithographic printing plate according to the DTR-process, etc.. From these disclosures it can not be inferred that the use of such compounds in dry toner particles in combination with a CCA would enhance the charging properties of the toner particles.

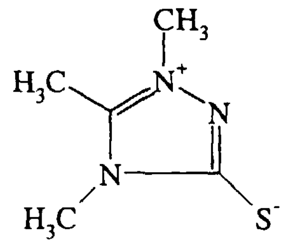
[0031] Preferred meso-ionic compounds for use in toner particles useful in the method of this invention correspond to the formula :



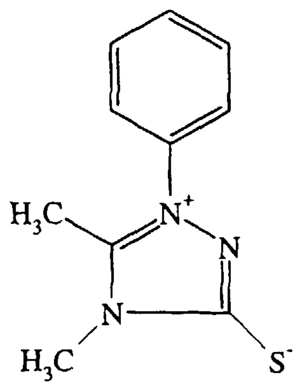
wherein R^1 and R^2 each independently represents an unsubstituted or substituted alkyl group, alkenyl group, cycloalkyl group, aralkyl group, aryl group or heterocyclic group, A represents an unsubstituted or substituted alkyl group, alkenyl group, cycloalkyl group, aralkyl group, aryl group, heterocyclic group or - NR^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.

[0032] Specific examples of 1,2,4-triazolium-3-thiolates suitable for use in accordance with the present invention are shown in table 1.

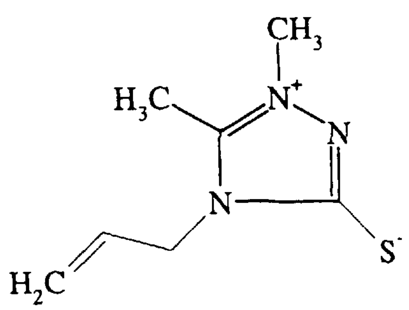
Table 1



(1)



(2)



(3)

[0033] Preferably at least 0.5 % by weight of said CLA is present in the toner particles, more preferably at least 1 % by weight.

[0034] 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 narrow charge distribution, i.e. the charge of the toner particles shows a distribution wherein the coefficient of variability (v), 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, e.g., US-A-5 569 567, US-A-5 622 803 and US-A-5 532 097 it is disclosed how to prepare both negatively and positively chargeable toner particles with narrow charge distribution. 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.

[0035] The invention thus not only encompasses a method for direct electrostatic printing, but also dry toner particles wherein a charge control agent (CCA) and a charge limitation agent (CLA) are incorporated. Preferably said CLA is a meso-ionic compound as described above. Preferably at least 0.5 % by weight of said CLA is present in the toner particles, more preferably at least 1 % by weight.

[0036] The invention also encompasses a device for direct electrostatic printing comprising :

- a charged toner conveyor bearing charged toner particles applied to it from a toner dispensing part carrying toner particles that have a charge control agent (CCA) and a charge limitation agent (CLA),
- one or more voltage sources for creating an electric field between the conveyor and an image receiving member, for forming a flow of charged toner particles to the image receiving member, and
- a printhead structure, placed in the flow and having printing apertures coupled to control electrodes coupled to a control voltage, being image wise modulated for image-wise depositing toner particles on the image receiving member.

[0037] Preferably said toner dispensing part is the sleeve of a magnetic brush carrying magnetic carrier particles and non-magnetic toner particles that have a charge control agent (CCA) and a charge limitation agent (CLA). The CLA is preferably a meso-ionic compound as described above.

Description of the DEP device

[0038] A non limitative example of a device according to this invention is shown in fig 1. It comprises :

(i) a means for bringing non magnetic charged toner particles (102a)to the surface of a charged toner conveyer (104), comprising a container (101) for two component developer (102), with non-magnetic toner particles (102a) and magnetic carrier particles (102b), a magnetic brush (103), with a magnetic core (103a) and a non-magnetic sleeve (103b). Said sleeve is equipped with a means (not shown in the figure) for rotating said sleeve, in the direction of arrow B so that the surface of the sleeve has a linear speed LSM. Said sleeve is coupled to a DC-voltage source DC1 and an AC-voltage source AC1 for jumping charged toner particles upon the surface of said charged toner conveyer (104) from said two component developer. The charged toner conveyer (104) is equipped with a means (not shown in the figure) for rotating said it, in the direction of arrow C, which is opposite to the direction of rotation of the sleeve of the magnetic brush, so that the toner bearing surface of it (104) has a linear speed LSC. The CTC is rotated so that the charged toner particles on its surface are brought in the development zone where a flow of charged toner particles (111) can be propelled while the magnetic brush (103) is located upstream of the development zone.

(ii) a back electrode (105) coupled to a DC-voltage source DC4, for maintaining said back electrode at a voltage different from the voltage (DC1/AC1) applied to the surface of the CTC, for forming an electrical propulsion field wherein a flow (111) of charged toner particles is created from the surface of the CTC towards the back electrode.

(iii) 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) coupled to a voltage source DC5 facing in the shown embodiment the CTC and a complex addressable electrode structure, hereinafter called "control electrode" (106a) around printing apertures (107) and coupled to a variable voltage DC3/AC3. Said printhead structure is placed in said flow of toner particles so that by applying a varying voltage DC3/AC3 to the control electrode the flow of toner particles towards the back electrode can be image-wise modulated in the development zone. 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.

(iv) conveyer means (108) to convey an image receiving member (a substrate) (109) between said printhead structure (106) and said back electrode (105) in the direction indicated by arrow A at a linear speed LSS,

(v) a spacer means (110), placed upon the front side of said printhead structure in order to keep the development nip between said charged toner conveyor and said printhead structure dynamically constant,

(vi) means for fixing (112) said toner onto said image receiving member.

[0039] 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 using toner particles according to the present invention, be different from the location shown in fig. 1.

[0040] Although in fig. 1 an embodiment of a DEP device using two electrodes (106a and 106b) on printhead 106 is shown, it is possible to implement a DEP device, using toner particles according to the present invention using devices with different constructions of the printhead (106). It is, e.g. possible to implement a DEP device having a printhead comprising only one electrode structure as well as a device having a printhead comprising more than two electrode structures. The apertures in these printhead structures can have a constant diameter, or can have a broader entrance or exit diameter.

[0041] The back electrode (105) of this DEP device can also be made to co-operate 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-A-4,568,955 and US-A-4,733,256. The back electrode, co-operating with the printhead structure, can also comprise one or more flexible PCB's (Printed Circuit Board).

[0042] Between said printhead structure (106) and the charged toner conveyer (104) as well as between the control electrode around the apertures (107) and the back electrode (105) 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 DEP device according to the present invention, shown in fig 1. voltage DC1/AC1 is applied to the sleeve of the magnetic brush 103, voltage DC2/AC2 is applied to the surface of the charged toner conveyer 104, voltage DC5 to the shield electrode 106b, voltages $DC3/AC3_0$ up to $DC3/AC3_n$ for the control electrode (106a). The value of DC3/AC3 is selected, according to the modulation of the image forming signals, between the values $DC3/AC3_0$ and $DC3/AC3_n$, on a time basis or grey-level basis. Voltage DC4 is applied to the back electrode behind the toner receiving member. In other embodiments of the present invention multiple voltages $DC5_0$ to $DC5_n$ and/or $DC4_0$ to $DC4_n$ can be used.

[0043] The magnetic brush 103 preferentially used in a DEP device according to the present invention is of the type with stationary core and rotating sleeve.

[0044] In a DEP device, according to a preferred embodiment of the present invention, any type of known carrier particles and toner particles can successfully be used. It is however preferred to use "soft" magnetic carrier particles. "Soft" magnetic carrier particles useful in a DEP device according to a preferred embodiment of the present invention are soft ferrite carrier particles. Such soft ferrite particles exhibit only a small amount of remanent behaviour, characterised in coercivity values ranging from about 4 kA/m up to 20 kA/m (50 up to 250 Oe). Further very useful soft magnetic carrier particles, for use in a DEP device according to a preferred embodiment of the present invention, are composite carrier particles, comprising a resin binder and a mixture of two magnetites having a different particle size as described in EP-B 289 663. The particle size of both magnetites will vary between 0.05 and 3 µm. The carrier particles have preferably an average volume diameter (d_v50) between 10 and 300 µm, preferably between 20 and 100 µm. More detailed descriptions of carrier particles, as mentioned above, can be found in EP-A-675 417.

[0045] It is preferred to use in a DEP device according to the present invention, toner particles with an absolute average charge over mass ratio (|q/m|) corresponding to $5\ \mu C/g \leq |q/m| \leq 15\ \mu C/g$, preferably to $8\ \mu C/g \leq |q/m| \leq 11\ \mu C/g$. The charge to mass ratio of the toner particles is measured by mixing the toner particles with carrier particles, and after 15 min of charging the q/m-ratio is measured as described in US-A-5 880 760. Said toner particles were pulled under vacuum from said CTC-roller to an accurately weighted filter paper (weight was WP in g), which was shielded in a Faraday cage. The amount of charge that arrived, after about 5 minutes vacuum pulling and after an accurate surface area of said CTC-roller was cleaned from said toner particles, at said filter paper was measured with a Coulomb meter in µC. The filter paper with the toner particles was weighted again, giving weight WPT in g. The charge to mass ratio was then determined as µC/(WPT-WP). In this disclosure the charge to mass ratio is taken as the absolute value, as a DEP device according to this invention can function either with negatively charged toner particles or with positively charged toner particles depending on the polarity of the potential difference between DC1/AC1 and DC4. Preferably the toner particles used in a device according to the present invention have an average volume diameter (d_v50) between 1 and 20 µm, more preferably between 3 and 15 µm. More detailed descriptions of toner particles, as mentioned above, can be found in EP A 675 417 that is incorporated herein by reference.

[0046] 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.

[0047] 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 DC3/AC3 applied on the control electrode 106a or by a time modulation of DC3/AC3. 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 DC3/AC3, applied on the control electrode.

[0048] 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 EP-A-634 862 with title "Screening method for a rendering device having restricted density resolution". This enables the DEP device, according to the present invention, to render high quality images.

EXAMPLES

The carrier particles

[0049] A macroscopic "soft" ferrite carrier consisting of a MgZn-ferrite with average particle size 50 µm, a magnetisation at saturation of 36 Tm^3/kg (29 emu/g) was provided with a 1 µm thick acrylic coating. The material showed virtually no remanence.

The toner particles

Comparative toner (CT1)

[0050] 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 x 10^{16} ohm.cm was 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 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-A-94/027192.

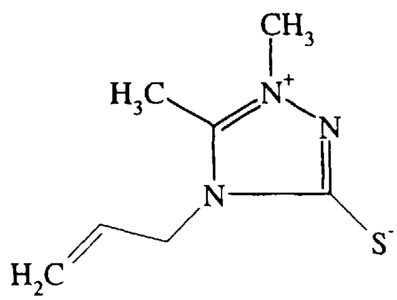
[0051] After cooling, the solidified mass was pulverised and milled using an ALPINE Fliessbettgegenstrahlmühle type 100AFG (trade name) and further classified using an ALPINE multiplex zig-zag classifier type 100MZR (trade name). The average particle size was measured by Coulter Counter model Multisizer (trade name), 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) and hydrophobic colloidal titaniumoxide particles.

Comparative toner 2 (CT2)

[0052] 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)

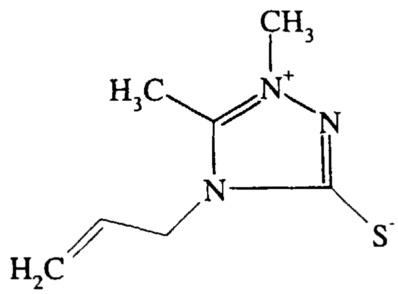
[0053] The third comparative toner was equal to comparative toner 1 (CT1) except for the addition of 2 % by weight of a charge limitation agent (CLA), with formula



to the bulk of the toner particles.

Invention toner 1 (IT1)

[0054] 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)

[0055] 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)

[0056] 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)

[0057] 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 (IT5)

[0058] 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, an experimental hybrid resin comprising polyester and polystyrene, provided by KAO Corp. Of Japan, was used.

Invention toner 6 (IT6)

[0059] 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, AG11, an experimental linear polyester, provided by KAO Corp. of Japan,was used.

The developer

[0060] An electrostatographic developer was prepared by mixing said mixture of toner particles and colloidal silica in a 5 % ratio (wt/wt) with silicon coated carrier particles.
The developers were used in a DEP device as described hereinbelow

The printhead structure (106)

[0061] A printhead structure (106) was made from a polyimide film of 50 μm thickness, double sided coated with a 5 μm thick copper film. The printhead structure (106) had two rows of printing apertures. On the back side of the printhead structure, facing the image receiving member, a rectangular shaped control electrode (106a) was arranged around each aperture. Each of said 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 (106b) was arranged around the aperture zone leaving a free polyimide zone of 1620 μm. Said 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 said printhead structure.

The charged toner conveyer (CTC)

[0062] 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

[0063] Charged toner particles were propelled to this conveyer from a stationary core (103a)/rotating sleeve (103b) type magnetic brush (103) 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.

[0064] 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 (103a), 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 said CTC (104).

[0065] The sleeve (103b) of said magnetic brush had a diameter of 20 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 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 (DC1) of +140 V. The surface of the charged toper conveyor was positioned at 750 μm from the surface of the magnetic brush, and said surface of said charged toner conveyor was connected to an AC power supply (AC2) with a sinusoidally oscillating field of 1800 V (peak to peak) at a frequency of 3.0 kHz with +100 V DC-offset (DC2). The surface of said charged toner conveyor was set via PU spacers means at 260 μm from said 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.

PRINTING EXAMPLES 1-9 (PE1-9)

[0066] In these experiments the toner particles as described above (CT1 to CT3 and IT1 to IT6) were used in a developer as described above. After putting a developer comprising 5 % of said toner particles in said 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 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

Table 1: (continued)

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
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

[0067] From the data in table 1 it is clear that only the combination of combining both a charge controlling agent (CCA) enhancing the charging kinetics, AND a charge limiting agent (CLA) limiting the maximum charge to mass ratio, an acceptable printing reliability regarding maximum printing density can be obtained. 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.

[0068] 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.

[0069] It must be clear for those skilled in the art that many other implementations of charging and limiting operations can be provided without departing from the spirit of the present invention.

Claims

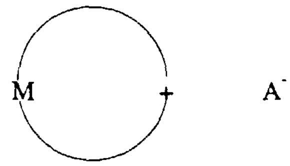
1. A method for Direct Electrostatic Printing (DEP) comprising the steps of :

- providing charged toner particles having an average charge to mass ratio Q1/m on an outer sleeve of a charged toner conveyor,
- adapting said toner particles so that after 30 seconds of printing said average charge to mass reaches a value of Q2/m, said value after 1 hour of printing changing by a factor of not more than 1.400,
- creating an electric field between said conveyor and an image receiving member, for attracting charged said toner particles to said image receiving member, and
- 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.

2. A method according to claim 1, wherein in said step of providing charged toner particles having an average charge to mass ratio Ql/m on an outer sleeve of a charged toner conveyor said toner particles are provided by a magnetic brush carrying magnetic carrier particles and non-magnetic toner particles.

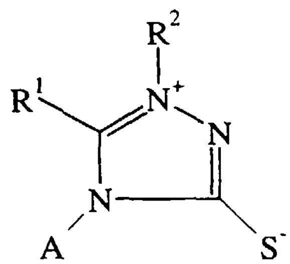
3. A method according to claim 1 or 2, wherein in said step adapting said toner particles said toner particles are adapted by incorporating in said toner particles both a charge control agent (CCA) and a charge limitation agent (CLA).

4. A method according to claim 3, wherein said charge limitation agent is a meso-ionic compound corresponding to the formula



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, an alkenyl group, an alkynyl group, an aralkyl group, an aryl group or a heterocyclic group.

5. A method according to claim 3, wherein said charge limitation agent corresponds 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.

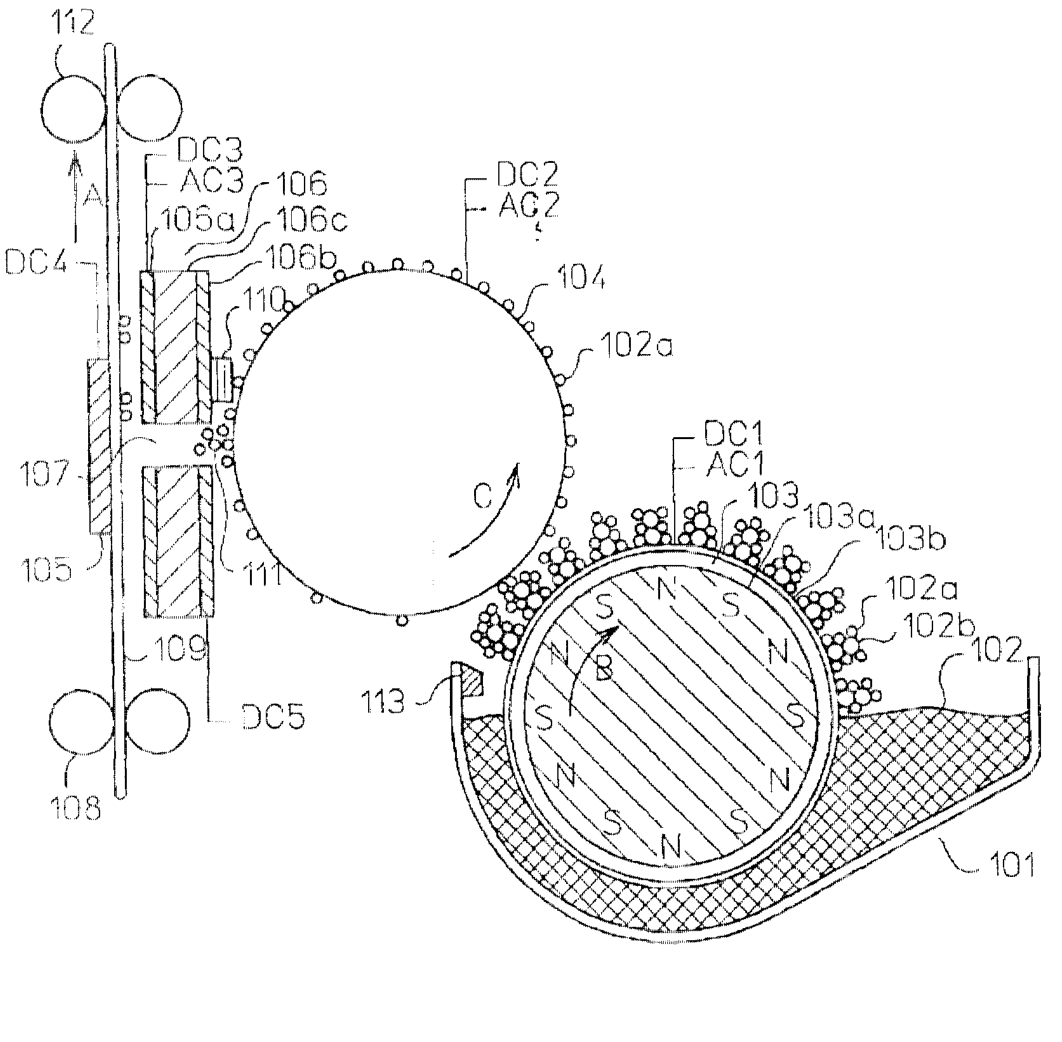
6. A method according to any of claims 3 to 5, wherein said charge limitation agent is present in said toner particles for at least 0.5 % by weight.

7. A device for direct electrostatic printing comprising :

- a charged toner conveyor bearing charged toner particles applied to it from a toner dispensing part carrying toner particles, adapted so that after 30 seconds of printing said toner particles have an average charge to mass reaching a value of Q2/m, said value after 1 hour of printing changing by a factor of not more than 1.400,
- one or more voltage sources for creating an electric field between the conveyor and an image receiving member, for forming a flow of charged toner particles to the image receiving member, and
- a printhead structure, placed in the flow and having printing apertures coupled to control electrodes coupled to a control voltage, being image wise modulated for image-wise depositing toner particles on the image receiving member.

8. A device according to claim 7, wherein said toner dispensing part carries toner particles comprising both a charge control agent (CCA) and a charge limitation agent (CLA).

9. A device according to claim 7 or 8, wherein said toner dispensing part is a sleeve of a magnetic brush carrying said toner particles together with magnetic carrier particles.


112
DC3
AC3
106
A
105a
106c
DC4
106b
110
DC2
AC2
104
102a
107
105
111
C
DC1
AC1
103
103a
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102b
102
N
S
B
109
113
DC5
108
101

Fig. 1

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 20 3349

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.7)
Y,D	US 4 755 837 A (SCHMIDLIN FRED W ET AL) 5 July 1988 (1988-07-05) * the whole document *	1-5,7-9	G03G15/34 G03G9/097
Y	PATENT ABSTRACTS OF JAPAN vol. 010, no. 358 (P-522), 2 December 1986 (1986-12-02) & JP 61 156141 A (RICOH CO LTD), 15 July 1986 (1986-07-15) * abstract *	1-5,7-9	
A	EP 0 715 218 A (AGFA GEVAERT NV) 5 June 1996 (1996-06-05) * abstract; figures *	1,7	
A	US 4 554 233 A (HASHIMOTO MITSURU ET AL) 19 November 1985 (1985-11-19) * claims *	4,5	

TECHNICAL FIELDS SEARCHED (Int.Cl.7)
G03G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	7 March 2000	Lipp, G

CATEGORY OF CITED DOCUMENTS

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The members are as contained in the European Patent Office EDP file on
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07-03-2000

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4755837 A	05-07-1988	CA 1308900 A	20-10-1992
		CN 1016823 B	27-05-1992
		DE 3789488 D	05-05-1994
		DE 3789488 T	14-07-1994
		EP 0266960 A	11-05-1988
		JP 2933930 B	16-08-1999
		JP 63123060 A	26-05-1988
JP 61156141 A	15-07-1986	NONE	
EP 0715218 A	05-06-1996	DE 69409533 D	14-05-1998
		DE 69409533 T	12-11-1998
		JP 8272135 A	18-10-1996
		US 5633110 A	27-05-1997
US 4554233 A	19-11-1985	JP 1667523 C	29-05-1992
		JP 3032786 B	14-05-1991
		JP 59078365 A	07-05-1984
		GB 2129577 A,B	16-05-1984

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82