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(54) **A method and device for direct electrostatic printing (DEP).**

(57) A method for direct electrostatic printing (DEP) on an intermediate substrate or on a final substrate is provided, using a device that comprises a back electrode (5), a printhead structure (6) comprising a control electrode in combination with apertures (7), a toner delivery means (1) presenting a cloud (4) of toner particles in the vicinity of said apertures (7), characterised in that

- (i) a multi-component developer is used comprising at least toning particles (toner particles) and magnetic attractable carrier particles and
- (ii) said toner delivery means is a magnetic brush assembly and said toner cloud is generated directly from said multi-component developer present at the surface of said magnetic brush assembly and
- (iii) said toner cloud is generated by an oscillating field.

The reference surface of said magnetic brush assembly is placed a distance (l) from the surface of the printhead structure facing said magnetic brush assembly, wherein l fulfils the condition :

$$2/3 L < l < 1000 + L$$

wherein all dimensions are expressed in  $\mu\text{m}$  and L is defined as the maximum thickness of the developer layer on said magnetic brush assembly in the absence of said oscillating field.

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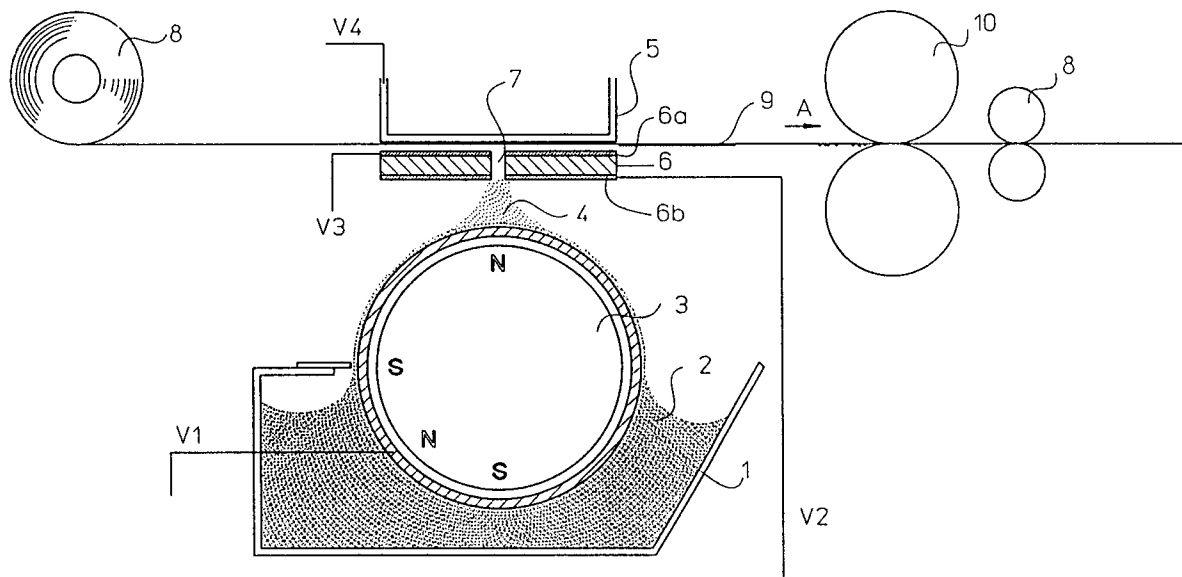


Fig. 1

## 1. Field of the invention.

This invention relates to the process of electrostatic printing and more particularly to Direct Electrostatic Printing (DEP). In DEP electrostatic printing is performed directly on a substrate by means of electronically addressable printheads.

## 2. Background of the Invention.

In DEP (Direct Electrostatic Printing) the toner or developing material is deposited directly in an imagewise way on a substrate, the latter not bearing any imagewise latent electrostatic image. The substrate can be an intermediate, in case it is preferred to transfer said formed image on another substrate (e.g. aluminum, etc.), but it is preferentially the final receptor, thus offering a possibility to create directly the image on the final receptor, e.g. plain paper, transparency, etc.... after 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 and in which either the powder image is fused directly to said charge retentive surface, which then results in a direct electrographic print, or in which the powder image is subsequently transferred to the final substrate and then fused to that medium, the latter process resulting in an indirect electrographic print. The final substrate can be different materials, such as a transparent medium, opaque polymeric films, 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 US-P 3,689,935. This document discloses an electrostatic line printer comprising a multilayered particle modulator or printhead comprising a layer of insulating material, a continuous layer of conductive material on one side of the layer of the insulating material and a segmented layer of conductive material on the other side of the layer of the insulating material. The printhead comprises also at least one row of apertures. Each segment of the segmented layer of conductive material is formed around a portion of an aperture and is insulatively isolated from each other segment of the segmented conductive layer. Selected potentials are applied to each of the segments of the segmented conductive layer while a fixed potential is applied to the continuous conductive layer. An overall applied field projects charged particles through a row of apertures of the particle modulator (printhead) and the intensity of the particle stream is modulated according to the pattern of potentials applied to the segments of the segmented conductive layer. The modulated stream of charged particles impinges upon a print-receiving medium interposed in the modulated particle stream and translated in a direction relative to the particle modulator (printhead) to provide a line-by-line scan printing. The segmented electrode is called the control electrode and the continuous electrode is called the shield electrode. The shield electrode faces, e.g., the toner supply and the control electrode faces the image recording member. A DC field is applied between the printhead and a backing electrode so as to attract the toner to the imaging receiving member that is placed between the printhead and the backing electrode.

Several modifications have been proposed to this basic principle, mainly to overcome four major problems :

- presenting an uniform cloud of toning particles to the printhead.
- supplying sufficient charged toning particles to the printhead structure, without scattering them or without contaminating the printhead structure and the engine environment.
- prevent clogging of the apertures in the printhead structure
- avoiding the deposition of wrong sign particles on the printhead structure, the repelling state for particles with the right sign corresponds to an attraction state for wrong sign particles.

In GS 2,108,432 different measures are disclosed to overcome some of the mentioned problems. Means are disclosed for realising a stable and uniform supply of toner particles to the printhead structure and for avoiding clogging of the apertures in the printhead structure by toner particles. Therefore a conveying member is provided on which a layer of toner particles is deposited and an AC voltage is applied between the toner conveying member and the continuous layer of conductive material on the printhead structure. Due to this AC voltage the toner particles "jump" between the toner conveying member and the surface of the printhead facing said toner conveying member, forming a "toner-cloud". The AC-voltage is adjusted such as to allow the toner particles to reach the printhead structure, thus enabling the overall DC voltage laid between the printhead structure and the substrate bearing member to extract said toner particles after modulation from said powder cloud. The overall DC voltage propels the toner particles, after said modulation, onto the image receiving member interposed between the printhead and a backing

electrode.

It is believed that the 'touching' toner particles will assist in delaying the contamination of the printhead structure and clogging of the apertures. At the same time a special design of the apertures in the printhead structure and a special selection of the material from which the printhead structure is made is claimed to assist in delaying the clogging. A last measure which is proposed is to 'clean' the printhead structure by periodical electrical bursts.

In DE-OS 3,411,948 an apparatus is disclosed wherein the toning particles are presented to the printhead structure in layer form on a conveying member. Said conveying member has a special design and AC/DC fields are used to realise jumping transport along said printhead structure. Also in this document the quality of the "toner-cloud" is addressed to make the process easier. This document teaches means to operate a DEP-system with larger distance between said conveying member and the printhead structure than before and enabling the use of lower electrical fields, in such a way that no disruptive discharge between the printhead structure and the backing electrode is possible. The toner is moreover continuously agitated such as to prevent clumping of the separate toner particles.

In EP-A 266 960 a toner delivery system is disclosed in which a monolayer of toner is deposited on the surface of the toner conveying means using a multi-component developer (carrier/toner) and a conventional magnetic brush. The use of a multi-component developer results in a favorable charge distribution in the toner and hence in a reduction of the contamination rate of the printhead.

In the disclosed system it is possible to clean the printhead by applying an AC voltage on the backing electrode in such a way that the very strong electrical AC field detaches clogged toner particles from the apertures of the printhead structure and repulses them to the conveying member. A set-up is necessary to recover the non-used toning material from said conveying belt and either dispose of it or reuse it by adding it back to the magnetic brush applicator used to deposit the active material on said conveying member.

In US-P 4,743,926 it is disclosed to use two toner conveying belts having a different charge to separate the toner particles as function of their charge and to bring only right sign toner to the printhead.

In US-P 4,912,489 a DEP device is disclosed wherein the control electrodes are positioned on the side of the printhead farthest away from the image recording member (and thus facing the toner supply) while the shield electrode is closest to the image recording member.

This unusual disposition of the shield and control electrode brings the advantage that only a low DC voltage is needed to modulate the flow of toner and that wrong sign toner accumulates in the vicinity of the toner supply and is not transported to the image receiving member.

In US-P 5,038,322 it is disclosed to have apertures in the printhead with smaller opening on the control electrode side than on the shield electrode side. This allows a smaller modulating current, prevents wrong sign toner accumulation and increases the toner cloud density.

In US-P 5,202,704 a DEP device is disclosed wherein the toner cloud is mechanically produced and the printhead is vibrated so as to free the apertures of the printhead from toner particles sticking within the apertures.

Also reference is made to Murata et al., in a paper presented at the Int. Conf. Appl. Electrostatics (Beijing, 1993), p 391 to 411. In this paper a DEP-engine is disclosed comprising a printhead structure composed of a matrix-electrode. The toner particles are metered on a conveying system, composed of a magnetic roller, and presented to said printhead structure. In this paper the limitations of the described DEP are discussed, and it is clearly shown that in the bulk of the toning material both low charged particles and wrong-sign particles are present. Both factors affecting adversely the performance and capability of DEP. Photographs presented in the mentioned paper and the data discussed in said paper, demonstrate the potential advantages of DEP as a recording method, but also indicate clearly its limitations.

The modification disclosed in the references cited above do solve, at least partially, the problems encountered in practicing DEP, but in most of the references rather complicated apparatus are necessary and the simplification of DEP, as compared to classical electrography, is not fully realized. Moreover, due to the fact that the intrinsic problems arising from the not sharply defined status of the charged toner cloud (presence of wrong-sign or too low charged particles) are not solved up to a high degree of satisfaction, the overall process will be limited in image quality and applications. Additionally there are described complex toner conveying means to present the marking toner particles to the printing and projection (toner cloud formation) zone. In all described systems the toner particles are presented in a layered form as single component material, this requires high quality and precision of both the electrical and mechanical construction of the DEP apparatus. Also the toner particles as such and the toner removing and reactivation means have to meet stringent requirements.

This illustrates again the complexity and the limitations of the hitherto described DEP systems.

There is thus still a need to have a system for practicing DEP, that while avoiding the problems cited above, is based on simpler apparatus and that yields high quality images in a reproducible and constant way.

### 5 3. Object of the invention

It is an object of the invention to provide a method for Direct Electrostatic Printing (DEP) that makes it possible to print high quality images in large edition without the need for cleaning the printhead structure.

It is another object of the invention to provide a device in which the method above can be executed.

10 It is a further object of the invention to provide toning particles for use in the method mentioned above.

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 intermediate substrate or on a final substrate, using a device that comprises a back electrode (5), a printhead structure (6) comprising a control electrode in combination with apertures (7), a toner delivery means (1) presenting a cloud (4) of toner particles in the vicinity of said apertures (7), characterised in that

15 (i) a multi-component developer is used comprising at least toning particles (toner particles) and magnetic attractable carrier particles and

(ii) said toner delivery means is a magnetic brush assembly and said toner cloud is generated directly from said multi-component developer present at the surface of said magnetic brush assembly and

20 (iii) said toner cloud is generated by an oscillating field.

In a preferred embodiment the reference surface of said magnetic brush assembly is placed at a distance (l) from the surface of the printhead structure facing said magnetic brush assembly, wherein l fulfils the condition :

$$25 \quad \frac{2}{3} L < l < 1000 + L$$

wherein all dimensions are expressed in  $\mu\text{m}$  and L is defined as the maximum thickness of the developer layer on said magnetic brush assembly in the absence of said oscillating field and measured according to TEST A. Hereinafter "reference surface of said magnetic brush assembly" is to be understood as the outer surface of the magnetic brush assembly when no developer is present on said outer surface.

30 In a further preferred embodiment, said toner particles used in the method of the present invention, have a average charge (q) expressed in fC such that  $1 \text{ fC} \leq q \leq 20 \text{ fC}$ , more preferably such that  $1 \text{ fC} \leq q \leq 10 \text{ fC}$ .

In an other preferred embodiment, said toner particles used in the method of the present invention, 35 have a charge distribution, measured according to TEST B, with a coefficient of variability,  $\nu$ , lower than 0.5, preferably lower than 0.33.

### 4. Brief Description of the Drawings

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

Fig. 2 represents a schematic cross-sectional drawing of an apparatus used in the determination of the above defined average charge and coefficient of variability of the charge distribution of charged toner particles.

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### 5. Detailed Description of the Invention

The modifications of the principle of DEP (Direct Electrographic Printing) have hitherto been addressed to the mechanical or electric parts of the devices, but little attention has been paid to the composition of the marking material, which will be called hereinafter the developer. It has been found that when a multi-component developer (i.e. comprising at least carrier particles and marking toner particles) is used, a significant improvement in DEP can be obtained. In this case said marking toner particles are subjected to the jet-process and said carrier particles, are associated to said toner particles on a conveyor means, but are not participating in the jet process itself.

55 It has been found that when a multi-component developer is used, and when its composition is adapted in a proper way, it is possible to perform DEP directly from a magnetic brush, which simplifies the construction of the DEP device by eliminating the need for a complex toner conveying means.

By adapting the thickness (L) of the developer layer of the magnetic brush (i.e. the length of the "hairs" of the magnetic brush) on the magnetic brush assembly to the distance (I) between the reference surface of said magnetic brush assembly and the printhead structure it is found that the electrical fields needed to perform the jetting process are within usefull ranges and that also obstruction of the apertures within the printhead structure can be markedly reduced. It has been found that both latter effects are improved when an oscillatory field interacts with the magnetic brush on said magnetic brush assembly.

The thickness, L, of the developer layer on the magnetic brush is measured according to TEST A.

#### TEST A

The thickness of the developer layer on the magnetic brush is determined as follows :

The developer is introduced within the developing unit. The unit is operated for 5 minutes in order to establish a steady state situation. Then the developing unit is mounted on a reference rack, containing a reference plane parallel to the axis of the magnetic brush assembly, and provided with a micrometer screw allowing to adjust the distance between the surface of the sleeve of the magnetic brush assembly and the reference plane and thus enabling to read the distance between both bodies with an accuracy of 10  $\mu$ m.

Then the development unit is operated with the normal settings, the development unit is stopped and the sleeve is moved to the reference plane over such a distance that the tops of the hairs of the brush touch the reference plane. This touching is observed visually using a illumination through the slit. The distance is recorded, and the measurement is repeated 5 times. The average of these 5 measurements is denoted 'L', the thickness of the developer layer on the magnetic brush and is expressed in  $\mu$ m.

It is preferred that the reference surface of said magnetic brush assembly is placed at a distance (I) from the surface of the printhead structure facing said magnetic brush assembly, wherein I fulfils the condition:

$$2/3 L < I < 1000 + L$$

wherein all dimensions are expressed in  $\mu$ m and L is defined as the maximum thickness of the developer layer on said magnetic brush assembly in the absence of said oscillating field and measured according to TEST A.

It is most preferred to place the reference surface of said magnetic brush assembly is at a distance (I) from the surface of the printhead structure facing said magnetic brush assembly, wherein I fulfils the condition

$$L < I < 500 + L$$

wherein all dimensions are expressed in  $\mu$ m and L is defined as the maximum thickness of the developer layer on said magnetic brush assembly in the absence of said oscillating field and measured according to TEST A.

When adapting the properties of the carrier to the properties of the toner and to the properties of the magnetic brush assembly, it is possible to have a "smooth" layer of developer on the surface of the magnetic brush assembly.

When adapting the triboelectrical charging properties of toner and carrier it is moreover possible to obtain toner particles with a specific charge level and moreover with a sharp charge distribution, thus avoiding the production of wrong sign toner, so that it is no longer necessary to take special (electrical or mechanical) measures for avoiding wrong sign toner transfer. Both adaptations make the DEP process to become more reproduceable and tuneable.

#### Description of the DEP device

A device for implementing a DEP method according to the present invention comprises (fig 1):

(i) a toner delivery means (1), comprising a container for developer (2) and a magnetic brush assembly (3), this magnetic brush assembly forming a toner cloud (4)

(ii) a back electrode (5)

(iii) a printhead structure (6), made from a plastic insulating film, double sided coated with a metallic film. The printhead structure (6) comprises one continuous electrode surface, hereinafter called "shield electrode" (6b) facing in the shown embodiment the toner delivering means and a complex addressable electrode structure, herinafter called "control electrode" (6a) around apertures (7), facing, in the shown

embodiment, the toner-receiving member in said DEP device. The location of the shield electrode (6b) and the control electrode (6a) 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.

(iv) conveyer means (8) to convey an image receptive member (9) for said toner between said printhead structure and said back electrode in the direction indicated by arrow A.

(v) means for fixing (10) said toner onto said image receptive member.

Although in fig. 1 an embodiment of a device, useful for implementing a DEP method according to the present invention, using two electrodes (6a and 6b) on printhead 6 is shown, it is possible to implement a DEP method according to the present invention using devices with different constructions of the printhead (6). It is, e.g. possible to implement the DEP method according to the present invention with a device having a printhead comprising only one electrode structure as well as with a device having a printhead comprising more than two electrode structures. The DEP method according to the present invention can also be implemented by using a DEP device comprising a electrode mesh array as printhead structure. Such an electrode mesh array has been disclosed at IS&T's Ninth International Congress on Advances in Non-Impact Printing Technologies/Japan Hardcopy '93, October 4-8, 1993 Yokohama Japan and published in the program and proceedings book with international classification numbers ISNB 0-89208-1724 and ISSN 0916-8087 p. 509 ss.

Between said printhead structure (6) and the magnetic brush assembly (3) as well as between the control electrode around the apertures (7) and the back electrode (5) behind the toner receiving member (9) as well as on the single electrode surface or between the plural electrode surfaces of said printhead structure (6) different electrical fields are applied. In the specific embodiment of a device, to be used in a DEP method according to the present invention, shown in fig 1. voltage V1 is applied to the sleeve of the magnetic brush assembly 3, voltage V2 to the shield electrode 6b, voltages V3<sub>0</sub> up to V3<sub>n</sub> for the control electrode (6a). The value of V3 is selected, according to the modulation of the image forming signals, between the values V3<sub>0</sub> and V3<sub>n</sub>, on a timebasis or gray-level basis. Voltage V4 is applied to the back electrode behind the toner receiving member.

In a DEP device according to the present invention, said toner delivery means is a layer of multi-component developer on a magnetic brush assembly, and the toner cloud is directly extracted from said magnetic brush assembly and not via a conveyer belt or the like.

The back electrode, the printhead structure, the conveying means for the image receptive member and the fixing means in a DEP device according to the present invention can be constructed in any suitable way, as disclosed in, e.g., US-P 3,689,935, GB 2,108,432, DE-OS 3,411,948, EP-A 266 960, US-P 4,743,926, US-P 4,912,489, US-P 5,038,322, US-P 5,202,704 etc.

Optionally a special semiconductive layer is put on the surface of the back electrode to reduce uncontrolled electrical discharges.

Such a semiconductive layer can be, e.g. a layer of semiconductive rubbery material.

In an other embodiment of the present invention, the fixing means (10) are not incorporated, but the back electrode (5) is heated and thus acts also as fixing means for toner particles.

The magnetic brush assembly to be used in a DEP device according to the present invention can be either of the type with stationary core and rotating sleeve or of the type with rotating core and rotating or stationary sleeve. A clear description of typical development units of both type, the stationary core/rotating sleeve type and the rotating core/rotating or stationary sleeve type can be found in the Hitachi Metals publication, Hitachi components for electrophotographic printing systems, p.5 - p.11, published by Hitachi Metals, International Ltd., 2400 Westchester Avenue, Purchase, New York, 10577, USA. The rotating core type developing unit is commonly used for monocomponent developers. Its use for dual component systems has also been described, in some patent applications of Minolta Corp., e.g. US 4,600,675, US 4,331,757, US 4,284,702. Similarly the use of a rotating core type developing process is described in the publication by Matsushita Electronic Components Co. Ltd. on the Pana Fine Process (National Technical Report, Vol. 28, No. 4, Aug. 1982, p. 676).

When using a magnetic brush of the type stationary core/rotating sleeve, a small toner cloud is formed in the vicinity of the apertures of the printhead due to a DC-field between the sleeve of said magnetic brush assembly and the printhead structure, without the presence of an oscillating field. A sufficiently dense toner cloud, however, is only formed when as an oscillatory field an AC-field (i.e. an oscillating field of electrical nature) is combined with said DC-field between the sleeve of said magnetic brush assembly and the printhead structure.

When using a magnetic brush of the type rotating core/rotating sleeve the developer is transported over the magnetic brush assembly by the combination of two effects. The first effect is the typical movement for a stationary core magnetic brush assembly, i.e. the developer is transported over the magnetic brush

because all magnetic brush hairs are tumbling from one stationary magnetic pole to an other since the base of each hair is forced to follow the slightly roughened surface of the roller. The other effect is the movement due to the fact that the top of each hair is tumbling towards the magnetic pole which is moving into its direction. The hairs will tumble from each magnetic pole to the next as said poles pass underneath the developer.

These effects will induce both a high transport speed and a typical oscillatory behaviour in the developer a sufficiently dense toner cloud is formed in the vicinity of the apertures of the printhead due to a DC-field between the sleeve of said magnetic brush assembly and the printhead structure, without an additional AC-field combined with said DC-field between the sleeve of said magnetic brush assembly and the printhead structure.

The rotating magnetic core of the magnetic brush assembly already provides an oscillating field of magnetic nature, originating from changing magnetic fields induced by moving different magnetic poles beneath the surface of said magnetic brush assembly. The formation of a toner cloud can advantageously be enhanced by combining also an AC-field with said DC-field between the sleeve of said magnetic brush assembly and the printhead structure.

In the implementation of the present invention it is preferred to use two different carrier types, each adapted to the specific lay-out of the magnetic brush assembly. The adaptation is made in such a way as to obtain either a short haired brush or a very soft, somewhat thicker brush with a pronounced smooth appearance. It is believed that this smooth or short appearance is a factor that is favourable to the process described in the present invention.

#### Description of carrier particles for use in the present invention

For the stationary core/rotating sleeve type magnetic brush the carrier particles are preferably "soft" magnetic particles (Carrier A).

A first interesting embodiment of "soft" magnetic carrier particles to be used in a DEP process according to the present invention is offered within the range of the so called soft ferrite carrier particles. Such soft ferrite particles exhibit only a small amount of remanent behaviour, characterised in coercivity values ranging from about 50 up to 250 Oe. An other embodiment of "soft" magnetic carrier particles can be derived from metal based particles. Both types of "soft" particles constitute macroscopic large particles of uniform composition over the whole particle.

These particles may be used as such as well as in an resin coated version (Carrier A1 and A2).

It is also possible to use as "soft" magnetic carrier particles, to be used in a DEP process according to the present invention, composite magnetic particles with a pronounced soft magnetic character. These composite particles comprise essentially the same type of magnetically active materials as the macroscopic large particles, with the exception that the magnetically active material is used in a very fine, quasi microscopic, form, so called pigment form and are bonded together over some binding matrix to form the particles. The advantages of using said particles is twofold first the magnetic properties of carrier particles comprising microscopic magnetic pigments imbedded in a binder resin can easily be adjusted by changing the formulation of the composite and second carrier particles comprising microscopic magnetic pigments imbedded in a binder resin have a lower specific gravity, giving rise to lower wear of the particles due to lower mutual mechanical impact, thus extending the lifetime of the developer (Carrier A3).

As soft magnetic pigments a variety of materials can be used, which comprise magnetic metal pigments such as fine powder, Fe powder, other metals and/or alloys, as well as magnetic oxide pigments both pure iron-based, such as magnetite, mixed iron oxide, etc. and mixed oxide magnetic pigments, commonly referred to as ferrites of the soft type. Ferrites can be represented by the general formula:



wherein Me denotes at least one divalent metal such as  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Cd}^{2+}$ , furtheron doped with monovalent or trivalent ions. As a special case  $\text{FeO.FeO}_3$ , magnetite, can be mentioned. The pigments referred to as soft are characterized by a coercivity of at most 250 Oe, as found by applying the procedure described below.

The coercivity of a magnetic material is the minimum external magnetic force necessary to reduce the remanence  $B_r$  to zero while it is held stationary in the external field, and after the material has been magnetically saturated. A variety of apparatus and methods for the measurement of the coercivity of the carrier particles used according to our invention can be employed. For the present invention, a Princeton Applied Research Model 155 Vibrating Sample Magnetometer, available from Princeton Applied Research



Co., Princeton, N.J., is used to measure the coercivity of powder particle samples. The powder was mixed with a nonmagnetic polymer powder (90 percent magnetic powder : 10 percent polymer by weight). The mixture was placed in a capillary tube, heated above the melting point of the polymer, and then allowed to cool to room temperature.

- 5 The filled capillary tube was then placed in the sample holder of the magnetometer and a magnetic hysteresis loop of induced magnetism (in emu/gm) versus external field (in Oersted units) was plotted. During this measurement, the sample was exposed to an external field of 0 to 8000 Oersted.

When a powdered material is magnetically saturated and immobilized in an applied magnetic field H of progressively increasing strength, a maximum, or saturated magnetic moment,  $B_{sat}$ , will be induced in the material. If the applied field H is further increased, the moment induced in the material will not increase any further. When the applied field, on the other hand, is progressively decreased till zero, reversed in polarity and thereafter increased again, the induced moment B of the powder will ultimately become zero and thus be on the threshold of polarity reversal in induced moment. The value of the applied field H necessary to bring about the decrease of the remanence,  $B_r$ , to zero is called the coercivity  $H_c$  of the material. The described soft magnetic pigments to be used in carrier particles for the DEP method of the present invention using a stationary core/rotating sleeve magnetic brush assembly, exhibit a coercivity of less than 250 Oersted when magnetically saturated, preferably a coercivity of at most 200 Oersted and most preferably a coercivity of at most 100 Oersted.

As soft magnetic carrier particles it is preferred to use 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  $\mu\text{m}$ .

For the rotating core/rotating or stationary sleeve type magnetic brush the carrier particles are preferably "hard" magnetic particles (Carrier B).

Here again homoparticles as well as composite particles can be used. The homoparticles are preferably hard ferrite macroparticles.

By hard magnetic macroparticles are understood particles with a coercivity of at least 250 Oe, most preferably 1000 Oe, when magnetically saturated, the magnetisation being at least preferably 20 emu/g of carrier material. Useful hard magnetic materials include hard ferrites and gamma ferric oxide. The hard ferrite are represented by a similar composition as cited above, whereby specific ions such as Ba, Pb, or Sr are used as disclosed in US Patent No. 3,716,630.

However, it is preferred to use composite particles as they give a lower specific gravity and are more flexible in design. In this case the hard magnetic particles are present in a fine form, called pigment, but are essentially of the same chemical composition (Carrier B1).

The hard magnetic pigments then show a coercivity of at least 250 Oe, preferably at least 1000 Oe, and more preferably at least 3000 Oe. In this regard, while magnetic materials having coercivity levels of 3000 and 6000 Oersted have been found useful, there appears to be no theoretical reason why higher coercivity levels would not be useful.

Useful hard magnetic pigments include hard ferrites and gamma ferric oxide. The hard ferrites are represented by a similar composition as cited above, whereby specific ions such as  $\text{Ba}^{2+}$ ,  $\text{Pb}^{2+}$ , or  $\text{Sr}^{2+}$  are used as disclosed in US Patent No. 3,716,630.

Also composite carrier comprising a binder resin and a mixture of both "soft" and "hard" magnetic particles can be used as the "hard" magnetic carrier to be used in a DEP method according to the present invention. When using such a composite carrier it is preferred that said carrier particles comprise a mixture of magnetic pigment particles wherein a portion (A) of said pigment particles has a coercive force of more than 250 Oe and an other portion (B) of said magnetic pigment particles has a coercive force of less than 250 Oe, the weight ratio of said portions (A) and (B) being in the range of 0.1 to 10.

Although the exact value of the induced magnetic moment of the carrier particles has to be adapted to the specifics of the magnetic brush assembly, said carrier particles of Carrier A and Carrier B preferably have, independently of the type of magnetic brush used in a DEP device according to the present invention, an induced magnetic moment B between 10 and 100 emu/gm, more specifically between 20 and 75 emu/g based on the weight of the carrier, when present in a field of 1000 Oersted, after full magnetisation.

The typical particle size of the carrier particles (Carrier A as well as Carrier B) to be used in accordance with the present invention, can be chosen over a broad range. It is however useful to define the particle size small enough in order to increase the specific surface area of the carrier and hence its capability to offer a larger interacting surface to the toner particles. On the other hand some care should be taken not to go for too fine particles, as they might become too weakly bond to the magnetic field of the magnetic brush assembly. In such a case they may become airborne from the moving brush by centrifugal forces or may be stripped too easily in electrical fields or be lost from the brush by mechanical impact of the magnetic hairs

with interacting components of the marking engine e.g. the printhead structure. It has been found most favourable to use a particle size in the range of 20 to 200  $\mu\text{m}$  more specifically in the range of 40 to 150  $\mu\text{m}$ . The diameter refers to the typical volume average particle diameter of the carrier beads, as it may be determined by sieving techniques.

- 5 The carrier beads can be used as such, i.e. uncoated, or they may be coated with inorganic as well as organic or mixed coatings. Typical coating thickness is in the range of 0.5 to 2.5  $\mu\text{m}$ . The coating may be used to induce different properties such as for example triboelectrical charging, friction reduction, wear resistance, etc.....

#### 10 Description of toner particles for use in the present invention

The toner particles used in a DEP process according to the present invention can essentially be of any nature as well with respect to their composition, shape, size, and preparation method and the sign of their tribo-electrically acquired charge.

- 15 In a PEP process according to the present invention it is possible to use black toners and coloured toners. The toner composition can comprise charge controlling additives, flow regulating agents etc. Examples of useful toner compositions can be found in, e.g., EP 058 013, US-P 4,652,509, US-P 4,647,522, US-P 5,102,763.

- 20 The toner for use in combination with carrier particles in a DEP process according to the present invention can be selected from a wide variety of materials, including both natural and synthetic resins and charge controlling agents as disclosed e.g. in US-P 4,076,857 and 4,546,060.

The shape of the toner particles can be irregular, as is the case in ground toners, or spheroidal. Spheroidization may proceed by spray-drying or the heat-dispersion process disclosed in US-P 4,345,015.

- 25 In WO 91/00548 the use of a fine toner particles exhibiting specific particle size characteristics and flowing characteristics is described, such fine toner particles are very useful for the present invention.

- The toner particles according to the present invention have preferably an average volume diameter ( $d_{v,50}$ ) between 3 and 20  $\mu\text{m}$ , more preferably between 5 and 10  $\mu\text{m}$  when measured with a COULTER COUNTER (registered trade mark) Model TA II particle size analyzer operating according to the principles of electrolyt displacement in narrow aperture and marketed by COULTER ELECTRONICS Corp. Northwell  
30 Drive, Luton, Bedfordshire, LC 33, UK.

- The main problem encountered with toner particles for use in DEP is the presence of wrong sign toners. To avoid the occurrence of wrong sign toners, it is possible to give the toner particles in triboelectric contact with the carrier particles a very high charge (either positive or negative). This can be achieved by matching the toner resins with the composition and species present in the carrier (e.g. the coating of the  
35 carrier particles) with respect to their respective triboelectric properties.

Preferably the toner particles, to be used in the present invention, will acquire, upon triboelectric contact with the carrier particles, a charge ( $q$ ), expressed in fC (femtoCoulomb) and that can be either negative or positive, such that  $1 \text{ fC} \leq q \leq 20 \text{ fC}$ , more preferably such that  $1 \text{ fC} \leq q \leq 10 \text{ fC}$ .

- 40 It is possible to have fairly low charged toner particles and avoid wrong sign toner by having toner particles with very homogeneous charge distribution.

Preferably the toner particles useful according to the present invention contain:

- (1) at least one triboelectrically chargeable thermoplastic resin serving as binder having a volume resistivity of at least  $10^{13} \Omega\text{-cm}$ , and  
(2) at least one resistivity lowering substance having a volume resistivity lower than the volume resistivity  
45 of said binder,

wherein said substance(s) (2) is (are) capable of lowering the volume resistivity of said binder by a factor of at least 3.3 when present in said binder in a concentration of 5 % by weight relative to the weight of said binder, and wherein said toner powder containing toner particles including a mixture of said ingredients (1) and (2) under triboelectric charging conditions is capable of obtaining an absolute median ( $q$ ) charge value  
50 ( $x$ ) lower than 20 fC but not lower than 1 fC, and said toner powder under the same triboelectric charging conditions but free from said substance(s) (2) then has an absolute median  $q$  value ( $x$ ) at least 50 % higher than when said substance(s) (2) is (are) present, and wherein the distribution of the charge values of the individual toner particles is characterized by a coefficient of variation  $\nu \leq 0.5$ , preferably  $\leq 0.33$ .

Said coefficient of variation ( $\nu$ ) is the standard deviation ( $s$ ) divided by the median value ( $x$ ).

- 55 The spread of charge values of individual toner particles containing said ingredients (1) and (2) is called standard deviation ( $s$ ) which for obtaining statistically realistic results is determined at a particle population number of at least 10,000.

Said standard deviation divided by said median yields according to the present invention an absolute

number equal to or smaller than 0.5, when the median  $q$  value is expressed in fC and stems from a curve of a percentage distribution of frequency of occurrence of a same charge (in y-ordinate) versus number of observed toner particles (in x-abcissa), said median being the value of the x-coordinate at which the area under the curve is bisected in equal area parts.

5 The coefficient of variation ( $\nu$ ) is preferred since it is more useful and significant to measure the spread in relative terms than using the standard deviation ( $s$ ) alone; it is independent of the units in which the variate is measured, provided that the scales begin at zero [ref. Christopher Chatfield "Statistics for technology" A course in applied statistics - Third ed. (1986) Chapman and Hall Ltd, London, p. 33.].

The triboelectric properties of toner particles as described above are measured according to TEST B.

10

## TEST B

The triboelectric properties of toner particles are measured by means of a charge spectrograph apparatus operating as schematically shown in Fig. 2.

15 The apparatus involved is sold by Dr. R. Epping PES-Laboratorium D-8056 Neufahrn, Germany under the name q-meter". The q-meter is used to measure the distribution of the toner particle charge ( $q$  in fC) with respect to a measured toner diameter ( $d$  in  $10 \mu\text{m}$ ). The measurement result is expressed as percentage particle frequency (in ordinate) of same  $q/d$  ratio on  $q/d$  ratio expressed as fC/ $10 \mu\text{m}$  (in abcissa).

20 Referring to said Fig. 2 the measurement is based on the different electrostatic deflection according to their  $q/d$  ratio of triboelectrically charged toner particles making part of a bunch of toner particles carried by a laminar air flow in a long narrow tube 1 at a mean speed  $v_m$  while passing through an electrical field  $E$  maintained perpendicular to the axis of said tube 21 by a registration electrode plate 22 and plate electrode 23 of opposite charge sign with respect to the registration electrode. Said electrodes are forming a  
25 condensor with plate distance  $y$  (5 cm).

A bunch of triboelectrically charged toner particles is injected by air-pulse into said tube 21 from a little pot 24 containing an air injection inlet 25 and a certain amount of triboelectrically charged toner to be tested. The developer is composed of magnetic carrier particles mixed with toner particles. The carrier particles are retained in the pot 24 by means of a magnetic field stemming from an electromagnet situated at the bottom  
30 of the pot, whereas the toner particles are taken away in a laminar air flow.

In said arrangement all toner particles with constant ratio  $q/d$  deposit in said tube according to their charge sign on the electrode of opposite charge sign as a "toner spectrum line at a point "x" in the tube, so that  $q/d = f(x)$ .

35 The registered toner deposit at  $x = 0$  (obtained by deposition in the absence of laminar flow) is used for controlling the equipment and for easy analysis of the records obtained. At a plate distance of  $y = 50$  mm of said condensor for producing the electric field  $E$  the following equation may be used to determine the  $q/d$  value of toner particles deposited at different points "x".

$$q E = 3 \pi \eta v_m d y/x$$

40

where :

$q$  is in fC,  $E$  is the electric field in kV/y,  $d$  is in  $10 \mu\text{m}$  units,  $\pi$  is 3.14...,  $\eta$  is the air viscosity, and  $x$  and  $y$  are in mm.

When the air flow AF is expressed in litre/min the  $q/d$  value is calculated by the following equation :

45

$$q/d(\text{fC}/10 \mu\text{m}) = a 36 \text{ AF}(\text{ltr}/\text{min})/V(\text{kV}) x(\text{mm})$$

where :

50  $V$  is the voltage between the electrodes, and "a" is a correction factor for small broadness of the registration electrode.

By means of a photomicroscope (microscope coupled to CCD-video camera) operating with an image analyzer the quantity of deposited toner particles and the percentage of toner deposited at same place is determined.

From the median  $q/d$  value, the average charge of the toner particles is calculated by

55

$$q = \frac{q/d \times d_{v,50}}{10},$$

5

wherein  $d_{v,50}$  is expressed in  $\mu\text{m}$ .

For more detailed information how to operate said "q-meter" reference is made to its operation manual of March 1988.

10 Toner compositions showing a narrow charge distribution are disclosed in WO 94/029770, WO 94/027192 and WO 94/027191, these application are incorporated herein by reference.

For negatively chargeable as well as for positively chargeable toners, said substance (2) capable of lowering the volume resistivity of said binder by a factor of at least 3.3 when present in said binder in a concentration of 5 % by weight relative to the weight of said binder, is within the following classes of compounds :

- 15
- onium compounds,
  - metal salts containing relatively large (bulky) anionic groups
  - betaines
  - amino acids
  - metal complex compounds

20

  - ionically conductive polymers in which the polymer chain carries anionic groups, e.g. sulphonate groups,
  - non-ionic antistatic polyethers, and
  - electronically conductive polymers, e.g. polyanilines, polypyrroles and polythiophenes.

25 By the term "onium compounds" in the present invention is understood "compounds containing an organic cation" for the term is intended to cover not only compounds named with the use of the suffix "onium" but also "olium", "inium", "ylium", "enium", etc. (see Chemical Abstracts - Vol.56 (1962) January-June, Nomenclature, pages 59N to 60N).

30 However, within said cited classes not all compounds exhibit the required resistivity decrease. As mentioned above a concentration of 5 % by weight in the selected binder composition has to decrease thereof the volume resistivity by a factor of at least 3.3.

The measuring procedure for selecting the resistivity decreasing substance proceeds by a test R described hereinafter.

#### Test R

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The resin or resin mixture to be tested is melt-blended with the resistivity decreasing substance being added in an amount of 5 % by weight with respect to the resin mass. The melt-blending proceeds at 110 °C for 30 minutes using a laboratory melt-kneader Type W50H (sold by Brabender OGH Kulturstra E 51-55 D4100 Duisburg 1).

40 After melt-mixing the product is solidified and milled using a laboratory mill Type A10 (sold by Janke and Kunkel - Germany). The product is sieved over 63  $\mu\text{m}$  mesh. The fraction passing through is collected and compressed with a pressure of 10 ton full load for 1 minute to form a circular tablet having a diameter of 13 mm and height of 1.15 mm.

45 The conductivity is measured after conditioning at 20 °C and 50 % relative humidity for 24 h. The tablet is corona charged up to 1100 V and the conductivity is determined by taking the voltage after 10 minutes of charge decay and comparing it with the voltage at start. From said measurement the specific resistivity or volume resistivity  $\rho_s$  in Ohm.cm is determined by the following equation :

$$\rho_s = t / 3.3 \times 8.854 \times 10^{-14} \times \ln(U_a/U_b)$$

50

wherein :

$\rho_s$  = volume resistivity (ohm-cm)

t = time of charge decay (t = 10 minutes)

$U_a$  = charging potential at t = 0 minutes

55

$U_b$  = charging potential at t = 10 minutes

## Description of the developer composition useful in the invention

Toner particles and carrier particles, as described above are finally combined to give a high quality electrostatic developer.

5 This combination is made by mixing said toner and carrier particles in a ratio (w/w) of 1.5/100 to 15/100, preferably in a ratio (w/w) of 3/100 to 10/100. To enhance the flowability of the developer composition, according to the present invention, it is possible to mix toner particles, according to the present invention, with flow improving additives. These flow improving additives are preferably extremely finely divided inorganic or organic materials the primary (i.e. non-clustered) particle size of which is less than 50 nm.

10 Widely used in this context are fumed inorganics of the metal oxide class, e.g. selected from the group consisting of silica ( $\text{SiO}_2$ ), alumina ( $\text{Al}_2\text{O}_3$ ), zirconium oxide and titanium dioxide or mixed oxides thereof which have a hydrophilic or hydrophobized surface.

The fumed metal oxide particles have a smooth, substantially spherical surface and are preferably coated with a hydrophobic layer, e.g. formed by alkylation or by treatment with organic fluorine compounds.

15 Their specific surface area is preferably in the range of 40 to 400  $\text{m}^2/\text{g}$ .

In preferred embodiments the proportions for fumed metal oxides such as silica ( $\text{SiO}_2$ ) and alumina ( $\text{Al}_2\text{O}_3$ ) are admixed externally with the finished toner particles in the range of 0.1 to 10 % by weight with respect to the weight of the toner particles.

Fumed silica particles are commercially available under the tradenames AEROSIL and CAB-O-Sil being trade names of Degussa, Frankfurt/M Germany and Cabot Corp. Oxides Division, Boston, Mass., U.S.A. respectively. For example, AEROSIL R972 (tradename) is used which is a fumed hydrophobic silica having a specific surface area of 110  $\text{m}^2/\text{g}$ . The specific surface area can be measured by a method described by Nelsen and Eggertsen in "Determination of Surface Area Adsorption measurements by continuous Flow Method", Analytical Chemistry, Vol. 30, No. 9 (1958) p. 1387-1390.

25 In addition to the fumed metal oxide, a metal soap e.g. zinc stearate, as described in the United Kingdom Patent Specification No. 1,379,252, wherein also reference is made to the use of fluor containing polymer particles of sub-micron size as flow improving agents, may be present in the developer composition to be used in a DEP process according to the present invention.

A DEP method according to the present invention can be addressed in a way that enables it to give not only black and white, i.e. being operated in a "binary way" but also to give an image with a plurality of gray levels. Gray level printing can be controlled by either an amplitude modulation of the voltage V3 applied on the control electrode or by a time modulation of the voltage V3 applied on the control electrode. By changing the duty cycle of the time modulation at a specific frequency, it is possible to print accurately fine differences in gray levels. It is also possible to control the gray level printing by a combination of an amplitude modulation and a time modulation of the voltage V3, applied on the control electrode.

35 The improved stability of the DEP process, according to the present invention makes it also possible to operate it in a reproducible way at higher resolution by the fact that obstruction of the jetting process even in smaller apertures is strongly reduced.

This combination of the increased resolution and of the possibilities for multilevel half-toning techniques makes that the DEP process, according to the present invention, is able to give increased image quality images, without going into the design and construction of a complex, costly and unreliable apparatus.

It can be advantageous to combine a DEP device, according to the present invention, wherein the toner cloud is directly extracted from a magnetic brush assembly, in one apparatus together with a classical electrographic device, in which a latent electrostatic image on a charge retentive surface is developed by a suitable material to make the latent image visible. In such an apparatus the DEP device according to the present invention and the classical electrographic device are two different printing devices used to print both images with various gray levels and alphanumeric symbols and/or lines on one sheet of substrate. In such an apparatus the DEP device according to the present invention can be used to print fine tuned gray levels (e.g. pictures, photographs, medical images etc. that contain fine gray levels) and the classical electrographic device can be used to print alphanumeric symbols, line work etc. that do not need the fine tuning of gray levels. Such an apparatus combining a DEP device, according to the invention with a classical electrographic device the strenghts of both printing methods are combined.

## EXAMPLES

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In all examples the same printhead structure, described below was used.

A printhead structure was made from a polyimide film of 100  $\mu\text{m}$  thickness, double sided coated with a 15  $\mu\text{m}$  thick copperfilm. The printhead structure had one continuous electrode surface opposed to the toner

delivering means, and a complex addressable electrode structure facing the receptor surface. No third electrode was used in this particular example. The addressable electrode structure was made by conventional techniques used in the micro-electronics industry, and using photoresist material, film exposure, and subsequent etching techniques. No surface coatings were used in this particular example. The apertures were 150  $\mu\text{m}$  in diameter, being surrounded by a circular electrode structure in the form of a ring with a width of 225  $\mu\text{m}$  measured radially from the edge of the 150  $\mu\text{m}$  apertures. The apertures were arranged in such a way as to obtain a pitch of 100  $\mu\text{m}$ , giving an overall addressability of the image of 250 dpi. The electrodes could be changed in their potential individually, whereas other elements were connected to one electrical potential for their whole corresponding structure.

#### EXAMPLE 1 to 12

In examples 1 to 12 the toner delivery means is a stationary core/rotating sleeve type magnetic brush (Magbrush A) as described below.

#### Magbrush A

The development assembly comprised two mixing rods used to transport the developer through the unit and to mix toner with developer and one metering roller.

The magnetic brush assembly was constituted of the so called magnetic roller, which in this case contained inside the roller assembly a stationary magnetic core, showing 9 magnetic poles of 500 Gauss magnetic field intensity and with an open position to enable used developer to fall off from the magnetic roller. The magnetic roller contained also a sleeve, fitting around said stationary magnetic core, and giving to the magnetic brush assembly an overall diameter of 20 mm. The sleeve was made of stainless steel roughened with a fine grain to assist in transport ( $<50 \mu\text{m}$ ).

A scraper blade was used to force developer to leave the magnetic roller. And on the other side a doctoring blade is used to meter a small amount of developer onto the surface of said magnetic brush assembly. 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.

#### Carrier particles

Three types of carrier particles were used to perform DEP according to examples 1 to 12 :

1. Carrier A1, a macroscopic "soft" ferrite carrier.

Carrier A1 comprised a MgZn-ferrite with average particle size 50  $\mu\text{m}$ , a magnetisation at saturation of 29 emu/g and was provided with a 1  $\mu\text{m}$  thick acrylic coating. The material showed virtually no remanence.

2. Carrier A2, a macroscopic, uncoated, "soft" ferrite carrier.

Carrier A2 comprised an uncoated CuZn-ferrite with average particle size 50  $\mu\text{m}$ , a magnetisation at saturation of 33 emu/g. The material showed virtually no remanence.

3. Carrier A3, a "soft" composite carrier.

A mixture containing :

1) 185 parts of a partially crosslinked polyester of propoxylated bisphenol A polycondensed with a mixture of isophthalic acid and benzene-1,2,4-tricarboxylic acid characterized by a softening point of 132 °C (ring and ball method), glass transition temperature of 64 °C, and acid value 18 mg KOH/g,

2) 375 parts of spheroidal magnetite A having an oil absorption number of 16, having an average particle size of 0.5  $\mu\text{m}$ , magnetization saturation in emu/g of 81 and remanence in emu/g of 8.1, said magnetite being sold under the trade name BAYFERROX of Bayer AG, W.Germany, and

3) 440 parts of spheroidal magnetite B having an oil absorption number of 31, having an average particle size of 0.2  $\mu\text{m}$ , maximum saturation magnetization of 84 emu/g and remanence in emu/g of 8.2 said magnetite being sold under the trade name MAPICO Black 200 by Titan Kogyo, Japan, was melt-kneaded for 30 min at 162 °C.

After cooling the kneaded mass was pulverised in an impact mill and powder particles sizing between 36 and 100  $\mu\text{m}$  were separated by sieves of suited mesh.

The magnetic properties, viz. magnetisation at 1000 Oe in emu/g and coercitive force ( $H_c$ ) in Oe of the carrier were measured to be 53 emu/g and 97 Oe.

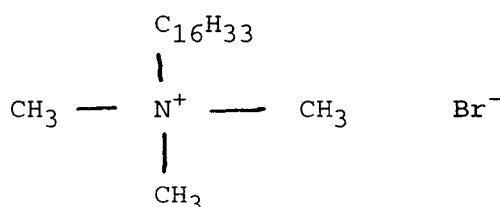
## Toner particles

In the printing experiments according to examples 1 to 12, following toner composition was used :

1. Toner T1 97 parts of a copolyester resin of fumaric acid and propoxylated bisphenol A, having an acid value of 18 and volume resistivity of  $5.1 \times 10^{16}$  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). As resistivity decreasing substance 0.5 % with respect to the binder of an onium salt K having the furtheron defined structural formula was added. By the test R described above it was found that the volume resistivity of the applied binder resin by mixing therewith 5 % of said onium salt K was lowered to  $5 \times 10^{14}$  ohm.cm which proves a high resistivity decreasing capacity (reduction factor :100).

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 resulting particle size distribution of the separated toner measured by Coulter Counter model Multisizer (tradename) was found to be 6.3  $\mu\text{m}$  average by number and 8.2  $\mu\text{m}$  average by volume. The average particle size by volume is represented hereinafter by  $d_{v,50}$ . 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  $\text{m}^2/\text{g}$ ).

## Onium salt K



## Triboelectric properties of the carrier and toner combinations

An electrostatic developer was prepared by mixing said mixture of toner particles and colloidal silica in a x % ratio (w/w) with carrier particles as defined above (in table 1 the various values of x are shown). The triboelectric charging of the toner-carrier mixture was performed by mixing said mixture in a standard tumbling set-up for 10 min. The developer mixture was run in the development unit (magnetic brush assembly Magbrush A) for 5 minutes after which the toner was sampled and the triboelectric properties measured according to TEST B described above.

Four developer mixtures were prepared and the triboelectric properties thereof measured. The results are summarized in Table 1.

TABLE 1

Developer	Toner conc. in %	$q/d$ fC/10 $\mu\text{m}$	$q$ fC	$v$
Carrier A1 + T1	4	-8.6	-7.1	0.13
Carrier A1 + T1	10	-4.6	-3.8	0.31
Carrier A2 + T1	4	-0.9	-0.75	0.50
Carrier A3 + T1	7	-3.5	-2.8	0.25

In table 1 is  $q = \frac{q/d \times d_{v,50}}{10}$ , wherein  $d_{v,50}$  is expressed in  $\mu\text{m}$ .

## EXAMPLE 1

Direct electrostatic prints were made using a developer comprising carrier A1 and 4 % w/w with respect to the carrier of toner T1, brought into magnetic brush assembly Magbrush A.

The brush appeared to be very thin and smooth. The thickness of the brush, measured according to TEST A, L, was 350  $\mu\text{m}$ .

Hereinafter the term "front side of the printhead structure" means the side of the printhead structure facing the sleeve of the magnetic brush assembly (i.e. the reference surface of the magnetic brush assembly).

The distance,  $l$ , between the front side of the printhead structure and the sleeve of the magnetic brush assembly, was set at 450  $\mu\text{m}$ .

The distance between the rear side of the printhead structure and the paper running over the back electrode was 150  $\mu\text{m}$  and the paper travelled at 2 cm/sec.

The electric potentials on the different electrodes were (referring to figure 1)

- at the sleeve of the magnetic brush V1 was set a 0 V DC, combined with an AC-field that was a square wave oscillating field of 3 kHz with a peak to peak amplitude of 2000 V
- at the shield electrode V2 was set at 0 V DC
- at the control electrode V3 was set at 0 V around every aperture and
- at the back electrode V4 was set at + 400 V.

In these conditions a solid black print was obtained, having a density of 1.80 in reflection. After a printing run of 8 consecutive hours no clogging nor contamination of the front electrode were observed. Also the control characteristics of the set-up were unchanged.

## EXAMPLE 2

Direct electrostatic prints were made in the same way as described in example 1, but at the control electrode V3 was set at - 175 V around every aperture.

In these conditions a homogeneous gray print was obtained, having a density of 0.80 in reflection. After a printing run of 8 consecutive hours no clogging nor contamination of the front electrode were observed. Also the control characteristics of the set-up were unchanged.

## EXAMPLE 3

Direct electrostatic prints were made in the same way as described in example 1, but at the control electrode V3 was set at - 350 V around every aperture.

In these conditions no toner deposition at all was observed.



#### EXAMPLE 4

Direct electrostatic prints were made in the same way as described in example 3, but at the control electrode V3 was set at - 350 V around every aperture, except for 1 aperture.

5 In these conditions a solid black, sharp delineated line with a width of 125  $\mu\text{m}$  was observed. The printing experiment ran again for 8 consecutive hours. After this timelapse no clogging nor contamination of the front electrode were observed. Also the control characteristics of the set-up were unchanged.

#### EXAMPLE 5

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Direct electrostatic prints were made in the same way as described in example 1, but at the control electrode V3 was switched between 0 and - 350 V around every aperture, with a frequency of 200 Hz and a 50 % duty cycle.

15 In these conditions a homogeneous gray print was obtained, having a density of 0.90 in reflection. The printing experiment ran again for 8 consecutive hours. After this timelapse no clogging nor contamination of the front electrode were observed. Also the control characteristics of the set-up were unchanged.

#### EXAMPLE 6

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Direct electrostatic prints were made in the same way as described in example 1, but at the sleeve of the magnetic brush assembly no AC-field was combined with the DC potential V1. The potential V1 was set at - 1500 V.

In these conditions no solid black print was obtained, but only an inhomogeneous gray print having a density of 0.40 in reflection.

25 The printing experiment ran again for 8 consecutive hours. After this timelapse no clogging nor contamination of the front electrode were observed. Also the control characteristics of the set-up were unchanged.

#### EXAMPLE 7

30

Direct electrostatic prints were made in the same way as described in example 1, but the distance, l, between the front side of the printhead structure and the sleeve of the magnetic brush assembly, was set at 275  $\mu\text{m}$ .

In these conditions proper functioning was possible. Only when the voltage V3 was raised to - 450 V, a small amount of carrier loss was observed.

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#### EXAMPLE 8

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Direct electrostatic prints were made in the same way as described in example 1, but the distance, l, between the front side of the printhead structure and the sleeve of the magnetic brush assembly, was set at 225  $\mu\text{m}$ .

In these conditions independently of the potential settings at the various electrodes, injection of the carrier particles in the printhead structure and onto the prints was observed, resulting in carrier loss and deterioration of the image.

45

#### EXAMPLE 9

Direct electrostatic prints were made in the same way as described in example 1, but the distance, l, between the front side of the printhead structure and the sleeve of the magnetic brush assembly, was set at 1500  $\mu\text{m}$ . Only when the AC-field that was combined with V1 at the sleeve of the magnetic brush was increased to 9,000 volts peak to peak toner deposition was observed. This high voltage impeded stable functioning of the power supply. Also the amount of deposited toner became unstable in the time.

#### EXAMPLE 10

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Direct electrostatic prints were made in the same way as described in example 1, but instead of using toner T1 at 4 % w/w with respect to the carrier, it was used at 10 % w/w. As can be seen from table 1, toner T1, in combination with carrier A1 at 10 % w/w has a lower charge and a wider charge distribution.

No prohibitive performance was found with respect to stability and clogging. However, to continue proper functioning for 8 consecutive hours with this low charge toner, the various potentials had to be increased by a factor of 1.6 as compared to the various potentials used in example 1, especially the AC-field forming the toner cloud had to be increased.

#### EXAMPLE 11

Direct electrostatic prints were made in the same way as described in example 1, but instead of using carrier A1, carrier A2 was used. As can be seen from table 1, toner T1 at a concentration of 4 % w/w, in combination with carrier A2, has a very small charge, a wide charge distribution, however without wrong sign particles.

The thickness of the developer layer on the sleeve of the magnetic brush assembly, L, was 500  $\mu\text{m}$  and the distance, I, between the reference surface of the magnetic brush assembly and the front side of the printhead structure was set at 750  $\mu\text{m}$ .

It was found that, due to the low charge of the toner particles, the electric potentials had to be raised to higher values. The AC-field had to be increased up to 4,000 V peak to peak, whereas in example 1 an AC-field corresponding to 2,000 V peak to peak gave good printing results. The higher voltages represented the upper limits for proper and stable functioning of the device. It is believed that the wide charge distribution influences adversely the stable functioning of the device.

#### EXAMPLE 12

Direct electrostatic prints were made in the same way as described in example 11, but instead of using carrier A2, carrier A3 was used. As can be seen from table 1, toner T1 at a concentration of 7 % w/w, in combination with carrier A3, has a charge that is intermediate between the charge of the toner particles used in example 1 and the charge of the toner particles used in example 11.

The thickness of the developer layer on the sleeve of the magnetic brush assembly, L, was 500  $\mu\text{m}$  and the distance, I, between the reference surface of the magnetic brush assembly and the front side of the printhead structure was set at 500  $\mu\text{m}$ .

In this case it was possible to have the device to function properly at acceptable potentials, but still all potentials had to be increased with a factor of 1.6 when compared to the potentials necessary in example 1. Again it was most important to increase the AC-field to assure proper functioning.

#### EXAMPLE 13

In this example the toner delivery means was a rotating core/rotating sleeve type magnetic brush (MagBrush B)

##### Magbrush B

A similar setup, as described under Magbrush A, was made with the exception that the internal magnetic core was symmetrical (8 poles of 750 Gauss) and had a diameter of 31.4 mm. The core was roated counterclockwise at 1500 rpm and the sleeve was rotated clockwise at 80 rpm. In said developing unit the doctoring blade was set at 500  $\mu\text{m}$  gap. A scraper was used to scrape of developer from said magnetic brush assembly and to get it refreshed with new developer inside the development unit.

##### Carrier particles

In this example a "hard" composite carrier was used.

##### Carrier B1

A mixture containing :

- (1) 19 parts of a partially crosslinked polyester of propoxylated bisphenol A polycondensed with a mixture of isophthalic acid and benzene-1,2,4-tricarboxylic acid characterized by a softening point of 132 °C (ring and ball method), glass transition temperature of 64 °C, and acid value 18 mg KOH/g,
- (2) 33 parts of a hard magnetic pigment having a Ba-containing ferrite structure with coercitive force of 3705 Oe, when magnetized, remanence of 31 emu/g and a saturation magnetisation of 61 emu/g, particle

size around 0,2  $\mu\text{m}$ ,

(3) 48 parts of a soft magnetic pigment having a magnetite structure with coercitive force of 130 Oe, when magnetised, remanence of 7 emu/g, saturation magnetisation of 78 emu/g, particle size around 0.5  $\mu\text{m}$ , was melt-kneaded for 30 min at 185°C. After cooling the kneaded mass was pulverized in an impact mill and powder particles sized between 25  $\mu\text{m}$  and 50  $\mu\text{m}$  were separated by appropriate sieving procedures.

The obtained particles were magnetically characterized after melting to a solid mass after magnetisation. A coercivity of 275 Oe and magnetic induction at 1000 Oe of 60 emu/g were measured. The carrier was magnetised up to saturation.

Toner particles

Toner T1 was used in this example.

Triboelectric properties of the carrier and toner combination

An electrostatographic developer was prepared by mixing a mixture of toner particles (toner T1) and colloidal silica in a 4 % w/w ratio with carrier particles (carrier B1) as defined above. The triboelectric charging of the toner-carrier mixture was performed by mixing said mixture in a standard tumbling set-up for 10 min. The developer mixture was run in the development unit (magnetic brush assembly Magbrush B) for 5 minutes after which the toner was sampled and the triboelectric properties measured according to TEST B described above.

Toner T1, in combination with carrier B gave following triboelectric properties (table 2) :

TABLE 2

Developer	Toner conc in %	q/d fC/10 $\mu\text{m}$	q fC	v
Carrier B1 + T1	4	-3.6	-2.9	0.25

In table 2 is  $q = \frac{q/d \times d_{v,50}}{10}$ , wherein  $d_{v,50}$  is expressed in  $\mu\text{m}$

#### EXAMPLE 13

Direct electrostatic prints were made using a developer comprising carrier B1 and 4 % w/w of toner T1, brought into magnetic brush assembly Magbrush B.

The brush appeared to be of intermediate thickness but very smooth. The thickness of the brush, measured according to TEST A, L, was 500  $\mu\text{m}$ .

Herinafter the term "front side of the printhead structure" means the side of the printhead structure facing the sleeve of the magnetic brush assembly.

The distance, l, between the front side of the printhead structure and the sleeve of the magnetic brush assembly, was set at 700  $\mu\text{m}$ .

The distance between the rear side of the printhead structure and the paper running over the back electrode was 150  $\mu\text{m}$  and the paper travelled at 2 cm/sec.

The electric potentials on the different electrodes were (referring to figure 1)

- at the sleeve of the magnetic brush V1 was set at - 200 V DC,
- at the shield electrode V2 was set at 0 V DC
- at the control electrode V3 was set at 0 V around every aperture and
- at the back electrode V4 was set at + 400 V. No AC-field was combined with the DC voltage V1 at the sleeve of the magnetic brush.

The sleeve of the magnetic brush rotated clockwise at 80 rpm and the core rotated counterclockwise at 1500 rpm.

In these conditions, although no AC-field was combined with the DC voltage V1 at the sleeve of the magnetic brush, a solid black print was obtained, having a density of 1.70 in reflection. The printing experiment ran for 8 consecutive hours. After this timelapse no clogging nor contamination of the front electrode were observed. Also the control characteristics of the set-up were unchanged.

This example demonstrates that no AC-field is necessary when a rotating core/rotating sleeve type magnetic brush is used. When a stationary core/rotating sleeve type magnetic brush is used the process does not function properly when no AC-field is present (cfr. example 6).

## Claims

1. A method for direct electrostatic printing (DEP) on an intermediate substrate or on a final substrate, using a device that comprises a back electrode (5), a printhead structure (6) comprising a control electrode in combination with apertures (7), a toner delivery means (1) presenting a cloud (4) of toner particles in the vicinity of said apertures (7), characterised in that
  - (i) a multi-component developer is used comprising at least toning particles (toner particles) and magnetic attractable carrier particles and
  - (ii) said toner delivery means is a magnetic brush assembly and said toner cloud is generated directly from said multi-component developer present at the surface of said magnetic brush assembly and
  - (iii) said toner cloud is generated by an oscillating field.

2. A method according to claim 1, wherein said printhead structure (6) comprises additionally a shield electrode.

3. A method according to claim 1 or 2, wherein the reference surface of said magnetic brush assembly is placed a distance (1) from the surface of the printhead structure facing said magnetic brush assembly, wherein 1 fulfils the condition :

$$2/3 L < l < 1000 + L$$

wherein all dimensions are expressed in  $\mu\text{m}$  and L is defined as the maximum thickness of the developer layer on said magnetic brush assembly in the absence of said oscillating field and measured according to TEST A.

4. A method according to claim 3, wherein said distance (1) fulfils the condition :

$$L < l < 500 + L$$

wherein all dimensions are expressed in  $\mu\text{m}$  and L is defined as the maximum thickness of the developer layer on said magnetic brush assembly in the absence of said oscillating field and measured according to TEST A.

5. A method according to any of the claims 1 to 4, wherein the back electrode (5) is heated.
6. A method according to any of the claims 1 to 5, wherein said toner particles have an average charge (q) wherein  $1 \text{ fC} \leq q \leq 20 \text{ fC}$ .
7. A method according to any of the claims 1 to 5, wherein said toner particles have an average charge (q) wherein  $1 \text{ fC} \leq q \leq 10 \text{ fC}$ .
8. A method according to any of the claims 1 to 7, wherein said toner particles have a charge distribution measured according to TEST B with a coefficient of variability,  $\nu$ , lower than 0.5.
9. A method according to any of the claims 1 to 7, wherein said toner particles have a charge distribution measured according to TEST B with a coefficient of variability,  $\nu$ , lower than 0.33

10. A method according to any of the claims 1 to 9, wherein said oscillating field is electrical in nature and originates from AC-fields.
- 5 11. A method according to any of the claims 1 to 9, wherein said oscillating field is magnetic in nature and originating from changing magnetic fields.
12. A method according to claim 11, wherein said changing magnetic field is induced by moving different magnetic poles beneath the surface of said magnetic brush assembly.
- 10 13. A method according to any of the claims 1 to 9, wherein said magnetic brush assembly is of the stationary core/rotating sleeve type.
14. A method according to claim 13 wherein said magnetically attractable carrier particles are soft composite particles exhibiting a coercivity of less than 250 Oe.
- 15 15. A method according to any of the claims 13 or 14, wherein said oscillatory field is an AC-field combined with a DC-field between the sleeve of said magnetic brush assembly and the printhead structure.
- 20 16. A method according to any of the claims 1 to 9, wherein said magnetic brush assembly is of the rotating core/rotating sleeve type.
17. A method according to claim 16, wherein said magnetically attractable carrier particles are hard composite particles exhibiting a coercivity of more than 250 Oe.
- 25 18. A method according to any of the claims 16 or 17, wherein said oscillatory field is magnetic and is provided by the rotating core of said magnetic brush assembly.
19. A method according to claim 18, wherein a AC-field is combined with a DC-field between the sleeve of said magnetic brush assembly and the printhead structure.
- 30 20. A method according to any of the claims 1 to 19, wherein gray level printing is controlled by amplitude modulation of voltage V3, applied to said control electrode.
- 35 21. A method according to any of the claims 1 to 19, wherein gray level printing is controlled by time modulation of voltage V3, applied to said control electrode (6a).
22. A method according to any of the claims 1 to 19, wherein said gray level printing by a combination of an amplitude modulation and a time modulation of the voltage V3, applied to said control electrode (6a).
- 40 23. A device for implementing a method for direct electrostatic printing (DEP) according to any one of the claims 1 to 22.
- 45 24. A DEP device according to claim 23 combined together with a classical electrographic device in one apparatus.

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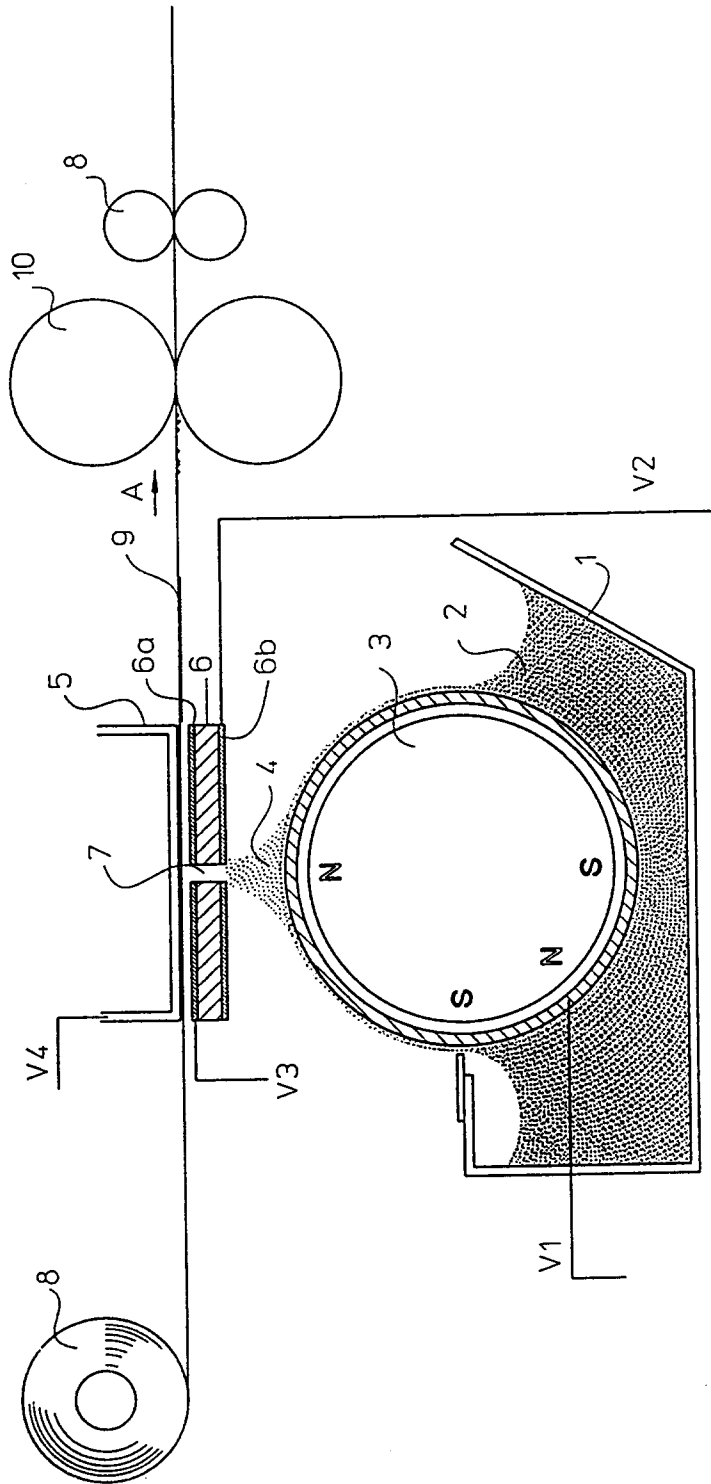


Fig. 1

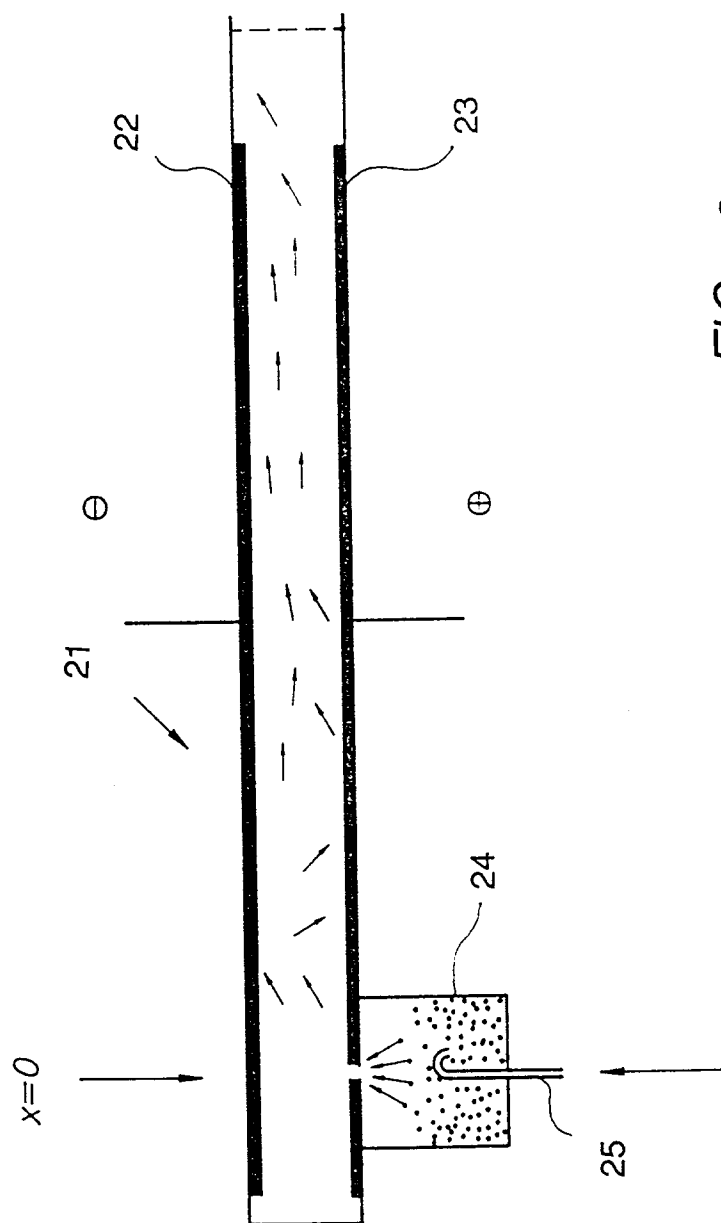


FIG. 2



European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number  
EP 95 20 0603

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.6)
Y	PATENT ABSTRACTS OF JAPAN vol. 10 no. 147 (P-460) [2204] ,29 May 1986 & JP-A-60 263962 (KONISHIROKU) 27 December 1985, * abstract *	1,2, 10-12, 16,18,23	G03G15/34
Y	--- PATENT ABSTRACTS OF JAPAN vol. 7 no. 177 (M-233) [1322] ,5 August 1983 & JP-A-58 081177 (CANON) 16 May 1983, * abstract *	1,2, 10-12, 16,18,23	
D,A	--- EP-A-0 266 960 (XEROX) * the whole document *	1,23,24	
A	--- US-A-5 132 708 (SCHMIDLIN)  * column 3, line 35 - column 6, line 40 *	1,10,23, 24	
A	--- US-A-5 233 392 (BROTHER) * abstract *	1,23,24	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
	-----		G03G
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 22 June 1995	Examiner Lipp, G
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