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# (54) Toner image with on top of it a radiation cured layer

(57) A toner image fixed on a substrate is provided characterized in that

i) said toner image comprises fused toner particles and
ii) said toner image comprises on top of it a non-image wise applied radiation cured layer, said layer having a thickness between 1 µm and 20 µm.

Said radiation cured layer is formed by applying a UV-curable composition on top of the toner image. A method and an apparatus for producing a toner image with on top of it a radiation cured layer are also disclosed.

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## Description

1. Field of the invention.

This invention relates to an electrostatographic imaging method. In particular this invention relates to a method to improve the mechanical properties of fixed toner images comprising several superimposed toner layers.

2. Background of the Invention

Electrostatic printing methods are manifold, e.g. Direct Electrostatic Printing, wherein electrostatic printing is performed directly from a toner delivery means on a receiving substrate, the latter not bearing any imagewise latent electrostatic image, by means of an electronically addressable printhead structure.

In another form of electrostatic printing toner images are made on an image-forming element in the form of a rotating drum provided with an electrostatic layer built up from a number of controllable electrodes in and beneath a dielectric layer. The voltage that is image-wise applied to said controllable electrodes attracts charged toner particles from a toner source.

It is also well known in the art of electrographic printing and electrophotographic copying to form an electrostatic latent image corresponding to either the original to be copied, or corresponding to digitized data describing an electronically available image.

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

In electrography an electrostatic latent image is formed by imagewise depositing electrically charged particles, e.g. from electron beam or ionized gas onto a dielectric substrate.

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

In magnetography a latent magnetic image is formed in a magnetizable substrate by a pattern wise modulated magnetic field. The magnetizable substrate must accept and hold the magnetic field pattern required for toner development which proceeds with magnetically attractable toner particles.

In toner development of latent electrostatic images two techniques have been applied : "dry" powder and "liquid" dispersion development of which dry powder development is nowadays most frequently used.

In dry development the application of dry toner powder to the substrate carrying the latent electrostatic image may be carried out by different methods known as, "cascade", "magnetic brush", "powder cloud", "impression" or "transfer" development also known as "touchdown" development described e.g. by Thomas L. Thourson in IEEE Transactions on Electronic Devices, Vol. ED-19, No. 4, April 1972, pp.495-511.

In the case of direct printing technologies, the toning developer is directly, image wise deposited on a final substrate to form a visible image. In the case of indirect printing methods a latent image, electrostatic or magnetographic, is developed to form a visible image. This visible image is the transferred, either directly or via an intermediate transfer medium, to a final substrate. In any case, the visible image of electrostatically or magnetically attracted toner particles, on the final substrate, is not permanent and has to be fixed by causing the toner particles to adhere to each other and the substrate by softening or fusing them followed by cooling. Normally fixing proceeds on more or less porous paper by causing or forcing the softened or fused toner mass to penetrate into the surface irregularities of the paper.

Dry-development toners essentially comprise a thermoplastic binder consisting of a thermoplastic resin or mixture of resins (ref. e.g. US-P 4,271,249) including colouring matter, e.g. carbon black or finely dispersed dye pigments or soluble dyes. The triboelectrically chargeability is defined by said substances and may, optionally, be modified with a charge controlling agent.

The toner image fixed to a substrate is vulnerable and can e.g. easily be scratched. Especially full colour images or black and white images wherein the tonal range is extended by the use of toner particles comprising different amounts of black pigment, are vulnerable, due to the height differences in the images. These height differences occur because of the superposition of various layers of toner particles depending on the colour hue or to the grey density that has to be reproduced. This "surface relief" enhances the possibility for mechanical scratches to occur in the image. It has been disclosed to apply a layer of colourless toner particles on top of the four colour toner image to protect the image and at the same time equalize the gloss of the image. Typical examples of such layers and different ways to apply such a layer are disclosed in, e.g., EP-A 629 921, EP-A 486 235, US 5,234,783, US 4,828,950, EP-A 554 981, WO 93/07541 and Xerox Research Disclosure Journal, Vol.16, N$^{o}$ 1, p. 69 (January/February 1991).

In European Application 96201373, filed on May 21, 1996, it is disclosed to apply on top of a toner image, a layer of silicone oil. The advantage of doing so is that the image is no longer easily scratched away and that the scratches that are only visible under some angles of illumination are also no longer formed.

It was however found that the measures that have been disclosed do indeed yield an improvement in scratchability, but further improvement of the physical properties of an image comprising fixed toner particles is still desirable.

## 3. Objects and Summary of the Invention.

It is an object of the invention to provide toner images, fixed on a final substrate, that are not sensitive to scratches.

It is a further object of this invention to provide multi-colour toner images, fixed on a final substrate, with or without a special top layer of toner particles, that are not sensitive to scratches.

It is a further object of the invention to provide toner images that are not sensitive to scratches and that have an even gloss, independently of the amount of superimposed toner layers.

It is still an other object of the invention to provide multi-colour toner images that are not sensitive to scratches and that have an even high gloss, independently of the amount of superimposed toner layers and of which the colours are rendered very vivid.

It is a further object of the invention to provide multi-colour images the colours of which are highly resistant to fading due to exposure to light.

It is an other object of the invention to provide a method and an apparatus for producing multi-colour toner images, with or without a special top layer of toner particles, that are not sensitive to scratches and have an even high gloss.

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

The objects of the invention are realized by providing a toner image fixed on a final substrate characterized in that i) said toner image comprises fused toner particles and ii) said toner image comprises on top of it a non-image wise applied radiation cured layer, said layer having a thickness between 1 μm and 20 μm.

## 4. Detailed Description of the Invention.

Toner images, fixed to a final substrate, often show a "surface relief", i.e. differences in height between different parts of the image. This is so in monochrome image where the image is formed by the presence or absence of toner particles on a substrate, but it is especially so in full colour images were different colours and hues are realized by the superposition of yellow, magenta, cyan and black (YMCK) toners. In such an image, the yellow parts are e.g. made up by one layer of toner particles and the black parts by the superposition of four layers of toner particles. This gives raise to differences in height in the image, furtheron referred to as "surface relief". In European Application 95202768, filed on October 13, 1995 it is disclosed to extend the grey scale (tonal range) in a black and white electrostatographic image fixed to a final substrate, by realizing the necessary different shades of grey with the superposition of toner particles comprising different amounts of black pigment. Also in these black and white images a surface relief is present. Toner images fixed on a final substrate and having a "surface relief" are quite sensitive to scratches.

It was found that by a non-image wise application of a layer of a radiation cured compound on a toner image and curing said compound, the image could be made very resistant to mechanical influences. Although this radiation curable composition can be either an electron beam curable composition or a UV-curable composition. The radiation curing can proceed off-line or on-line. When the curing proceeds off-line, there is no special preference for the curing method, when the curing proceeds on-line (i.e. in the electrostatographic printing apparatus itself), it is preferred in the present invention to use UV-curable compositions. When using a UV-curable compound (or a mixture of UV curable compounds) to form the radiation curable layer mentioned above, it proved that such an application, although being beneficial on all kind of toner images, was especially beneficial on multi-colour images. In such images, not only the physical strength of the image could be improved, but the images could be given an even high gloss and the colour could be rendered more vivid by the application of an UV-curable layer on top of the image.

Such a layer is applied in such a way that the dry thickness of it is between 1 μm and 20 μm, preferably between 4 and 12 μm. This thickness is achieved by applying between 1 g/m$^2$ and 20 g/m$^2$, preferably between 4 g/m$^2$ and 12 g/m$^2$ of radiation curable composition on the image.

An overview of radiation curable composition useful in the present invention can be found in EP-A 510 754 and a very comprehensive overview of radiation curable compositions and the commercial availability of compounds for said compositions can be found in the series "Chemistry and Technology of UV and EB formulation for coatings, inks and paints" edited by P.K.T. Oldring, published by SITA Technology, London SW18 4JQ, England 1991 (five volumes).

Very useful UV-curable compositions for forming a protective coating in the present invention contain as primary components :

(1) a cross-linkable prepolymer or oligomer,
(2) a reactive diluent monomer,
(3) a photoinitiator.

Optionally additives and pigments or dyes may be incorporated in the composition.

The components of the radiation curable composition for use in this invention are chosen such the components do not, or only in to small extent penetrate, in the toner particles forming the image. The penetration of the components in the toner particles can be measured as follows. On an fused toner image (mono-chrome or full colour) a 6 µm thick layer of the UV-curable composition under investigation, is applied by a bar coater. Then the layer is UV-cured for 0.5 sec with a high pressure mercury lamp giving an intensity of 80 W/cm. The gloss of the layer is measured with a in a Minolta Multi-gloss 268 reflectometer (trade name of Minolta, Osaka, Japan). When this gloss was higher than 80 %, the UV-curable composition is a useful composition according to the present invention. It seems that the penetration of the UV-curable composition decreases as the cure-rate of the composition increases.

The usual amounts of three primary components calculated on the total coating composition are 0-100 % by weight (% wt/wt), preferably between 5 and 90 % wt/wt for the prepolymer, 0-100 % wt/wt, preferably between 5 and 90 %wt/wt for the reactive diluent Optionally minor amounts (e.g. 5 % by weight) of non-reactive organic solvent for the prepolymer may be present. In UV-curable compositions according to the present invention the oligomer (or prepolymer) and the reactive diluent monomer together account for between 30 and 100 % by weight, preferably between 35 and 95 % wt/wt of the total composition. When an oligomer and a reactive diluent monomer are present in the radiation curable composition, then is the ratio between said oligomer (prepolymer) and said reactive diluent monomer, in compositions useful in the present invention, between 10:1 and 1:10, preferably between 5:1 and 1:5.

Useful prepolymers or oligomers

Examples of suitable prepolymers for use, either alone or in a mixture) in a radiation-curable composition applied according to the present invention are the following :

- unsaturated polyesters
- epoxy acrylates
- urethane acrylates
- polyester acrylates and
- acrylic acrylates/saturated resins.

Unsaturated polyesters, useful in UV-curable compositions according to this invention, are polyester comprising more than 40 mole percent of moieties derived from unsaturated dicarboxylic acids as, e.g. maleic acid, fumaric acid.

Epoxy acrylates are prepared by the reaction of an epoxy resin and acrylic or methacrylic acid. Preferably the epoxy acrylate resin comprises bisphenol 'A' diglycidyl ether moieties. Useful epoxyacrylate prepolymers are available in 100 % oligomer form as well as in a solution in a diluent reactive monomer. Typical 100 % oligomers are, e.g., ACTILANE 72 (trade name of Harcros Chemicals Ltd, Manchester, England), ACTOCRYL 100 (tradename of Anchor Chemical (UK), Manchester, England), EBECRYL 600, EBECRYL 3700, EBECRYL 3701 (trade names of UCB, Radcure Specialities, Drogenbos, Belgium), etc. Typical epoxyacrylates as prepolymer diluted in a diluent reactive monomer are, e.g. ACTILANE 7220 TP, (trade name of Harcros Chemicals Ltd, Manchester, England), wherein the diluent monomer is TriPropylene Glycol DiAcrylate (TPGDA), ACTOCRYL 10020 A, (tradename of Anchor Chemical (UK), Manchester, England), wherein the diluent monomer is also TPGDA, EBECRYL 604, wherein the diluent monomer is 1,6 HexaneDiol DiAcrylate (HDDA), EBECRYL 1940, wherein the diluent monomer is DiPropylene Glycol DiAcrylate (DGGDA) (EBECRYL is a trade name of UCB, Radcure specialities, Drogenbos, Belgium), etc.

Urethane Acrylates useful in the present invention can be prepared by the reaction of one or more organic mono- or poly-isocyanate compounds and an hydroxyacrylate or hydroxymethacrylate. These basic urethane acrylates can be modified by introducing in the reaction mixture other hydroxyl group comprising compounds together with one or more organic mono- or poly-isocyanate compounds and an hydroxyacrylate or hydroxymethacrylate. When the other hydroxyl group comprising compound is a diol or polyol, polyol urethane acrylates are produced; when said compound is a polyester with free hydroxylgroups, polyester urethane acrylates are formed; when said compound is a polyether polyol or diol, polyether urethane acrylates are formed. All modifications of the basic urethane acrylate compounds, are useful in the present invention. By using poly-isocyanate compounds, the acrylate functionality in the urethaneacrylate oligomer (prepolymer) can be enhanced. Typical very useful isocyanate compounds are, e.g., toluenediisocyanate, tetramethylenediisocyanate, hexamethylenediisocyanate, etc. Also the isocyanate compounds available through Bayer, Leverkusen, Germany under tradename DESMODUR are very useful for preparing urethaneacrylates to be used as oligomer in the present invention. Useful hydroxyacrylates for preparing said urethaneacrylates are, e.g. hydroxyethylacrylate, hydroxypropylacrylate, hydroethylmethacrylate, etc. Urethaneacrylates are preferred for use as oligomers (prepolymers) in a UV-curable composition according to the present invention. These prepolymers have excellent film forming characteristics and by proper choice of the oligomer a widely varying range of film properties can be realized. Also Polyester Urethane Acrylates can be useful as oligomer (prepolymer) in UV-curable compositions for use in the present invention. Typical useful polyester urethane acrylates in accordance with this invention, consist of three major components : a polyester polyol, i.e. a polyester with a high (> 2.5 mg KOH/g polyester) hydroxyl value, a multifunctional isocyanate and a hydroxyacrylate or hydroxymethacrylate. Also diol or polyol urethane acrylates can be used in the present invention, typical members of this group comprise a diol (ethylene glycol, 1,6 hexanediol, etc) and/or a polyol (glycerol, trimethylolpropane, etc), a multifunctional isocyanate and a hydroxyacrylate or hydroxymethacrylate. When a polyol is used the resulting urethane is a "hard" urethane acrylate, when a aliphatic diol is used (e.g. 1,6 hexanediol) the resulting urethane is a "soft" urethane acrylate. Thus by the proper choice of the reagents in preparing a polyol urethane acrylate, the hardness and the brittleness of a UV-cured layer of the polyol urethanes can be controlled. Several urethane acrylates are commercially available in 100 % oligomer form as well as in a solution in a diluent reactive monomer. Typical 100 % oligomers are, e.g., ACTILANE 17 (trade name of Harcros Chemicals Ltd, Manchester, England for a flexible aromatic urethane acrylate), ACTILANE 40 (trade name of Harcros Chemicals Ltd, Manchester, England for a hard aromatic urethane acrylate), ACTOCRYL 300 (tradename of Anchor Chemical (UK), Manchester, England, for a flexible aromatic urethane acrylate with functionality 2), EBECRYL 210 an aromatic urethane acrylate with functionality 2, EBECRYL 220 an aromatic urethane acrylate with functionality 6, EBECRYL 6700 an aromatic urethane acrylate with functionality 2.3, EBECRYL 270 a flexible aliphatic urethane acrylate with functionality 2 (EBECRYL is a trade name of UCB, Radcure Specialities, Drogenbos, Belgium), etc. Polyester urethane acrylates are, a.o., CRAYNOR CN 960 (trade name of Cray Valley - Radiation curing and Speciality Monomers, Puteaux, France for a hard polyester urethane acrylate), CRAYNOR CN 961 (trade name of Cray Valley - Radiation curing and Speciality Monomers, Puteaux, France for a resilient polyester urethane acrylate) and CRAYNOR CN 962 (trade name of Cray Valley - Radiation curing and Speciality Monomers, Puteaux, France for a flexible polyester urethane acrylate). PHOTOMER 6118 (trade name of Harcros Chemicals Ltd, Manchester, England) is a typical polyether urethane acrylate. Comparable compounds are available, from the same companies, as solution in a diluent reactive monomer, e.g. ACTILANE 182TP (trade name of Harcros Chemicals Ltd, Manchester, England for an aromatic urethane acrylate in TPGDA), ACTILANE 2020TP (trade name of Harcros Chemicals Ltd, Manchester, England for an aliphatic urethane acrylate in TPGDA), ACTOCRYL 330X (tradename of Anchor Chemical (UK), Manchester, England, for a resilient aliphatic urethane acrylate with functionality " in TPGDA), EBECRYL 204 an aromatic urethane acrylate with functionality 3 in HDDA, EBECRYL 224 an aliphatic urethane acrylate with functionality 2 in HDDA, EBECRYL 264 an aliphatic urethane acrylate with functionality 3 in HDDA, (EBECRYL is a trade name of UCB, Radcure Specialities, Drogenbos, Belgium), etc.

Polyester acrylates are prepared by the condensation of acrylic acid with hydroxyl groups on a polyol or a polyester backbone or by the reaction of hydroxy acrylate (hydroxymethacrylate) with residual acid groups on a polyester structure. In the synthesis polyesters showing a hydroxyl value and/or a carboxyl value > 2.5 mg KOH/g of polyester are beneficially used. Also polyester acrylates are commercially available in diluent free form or as a solution in a diluent reactive monomer. Typical examples of commercial diluent free polyester acrylates are EBECRYL 657 a tetrafunctional compound, EBECRYL 870 a hexafunctional compound, (EBECRYL is a trade name of UCB, Radcure Specialities, Drogenbos, Belgium), etc.

Acrylic resins are prepared by free radical polymerization and can proceed in four different techniques, bulk polymerisation, solution polymerisation, emulsion polymerisation and dispersion polymerisation. The bulk polymerisation is generally speaking quite impractical due to the exothermic nature of the free radical reaction. For the production of acrylic acrylates, acrylic resins with pendant functionality are first prepared and then reacted with e.g. an hydroxyacrylate or hydroxymethacrylate as described above for polyester acrylates and urethane acrylates. Monomers with functional groups and being suitable for incorporation in the acrylic resin are,e.g., acrylic acid, methacrylic acid, maleic anhydride, glycidylacrylate, dimethylamino acrylate, allyl isocyanate, methacrylamide, etc.

## Useful reactive diluent monomers

Reactive diluent monomers that preferably serve, either alone or in a mixture, as solvent for the prepolymers are chosen on the basis of several properties :

- low toxicity
- low volatility
- low viscosity
- high reactivity
- good mechanical properties and weatherability of a UV-cured layer comprising polymeric compounds derived from them.

Useful diluent monomers in accordance with the present invention can be monofunctional, difunctional or polyfunctional. Useful monofunctional diluent monomers are, e.g., methyl (metha)acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, glycidyl methacrylate, n-hexyl acrylate, lauryl acrylate, tetrahydrofurfurylmethacrylate and the like.

Mono-functional diluent monomers are not necessarily applied in conjunction with unsaturated prepolymers but can be used to form a radiation-curable composition with good abrasion resistance in conjunction with saturated polyesters, e.g. polyethylene terephthalate and polyethylene isophthalate. Preferred mono-functional monomers for use therewith are methyl methacrylate and tetrahydrofurfuryl methacrylate.

Examples of suitable di-functional monomers are :

1,6-hexanediol diacrylate, 1,6-hexanediol dimethacrylate, silicone diacrylate, neopentylglycol, 1,4-butanediol diacrylate, ethyleneglycol diacrylate, polyethyleneglycol diacrylate, pentaerythritol diacrylate, divinylbenzene.

Examples of suitable tri- or more-functional monomers are :

trimethylolpropane triacrylate, trimethylolpropane trimethacrylate, pentaerythritol triacrylate, dipentaerythritol hexaacrylate, an acrylate of ethylenediamine, aliphatic and aromatic urethane acrylates and the monomers according to general formula (I) described in European patent application No. 91200468.6 filed March 5, 1991, wherein reference is made for the preparation of said monomers to published German patent applications Nos. 3,522,005, 3,703,080, 3,643,216, 3,703,130, 3,703,080, 3,917,320 and 3,743,728.

The tri- or more functional diluent reactive monomers could also be classified with the oligomers useful in the present invention. Especially alkoxylated tetraacrylates (ATTA) and highly alkoxylated tetraacrylates (PPTTA) are considered to be rather oligomers. Therefore these compounds can be used in a radiation curable solution as oligomer (or prepolymer) and without the use of a diluent reactive monomer. Pentaacrylates, tetraacrylates and alkoxylated tetraacrylates (hereinafter for short : multiacrylates) have low viscosity, good flow characteristics and excellent cure-rates. A particularly useful property of these multiacrylates is the fact that they give very low irritation and have low odour. They can give hard though films with very good abrasion resistance. For all these reason said multiacrylates are very useful compounds in accordance with the present invention. Said multiacrylates have also the advantage that there is little or no penetration in the toner particles, so that a thin layer of UV-curable compound can be used to achieve the advantages of this invention, i.e. low scratchability, high even gloss, high solvent resistance and high weatherability. This thin layer has the advantage that the image on the substrate is made up of relatively thin layer, which decreases the possible brittleness of the image and improves the flexibility of the image.

## Useful photoinitiators

When the radiation-curing is carried out with ultraviolet radiation (UV), a photoinitiator is present in the radiation curable composition to serve as a catalyst to initiate the polymerization of the monomers and their optional cross-linking with the pre-polymers resulting in curing of the coated protective layer composition. A photosensitizer for accelerating the effect of the photoinitiator may be present.

Photoinitiators suitable for use in UV-curable coating compositions belong to the class of organic carbonyl compounds, for example, benzoin ether series compounds such as benzoin isopropyl, isobutylether; benzil ketal series compounds; ketoxime esters; benzophenone series compounds such as benzophenone, o-benzoylmethylbenzoate; acetophenone series compounds such as acetophenone, trichloroacetophenone, 1,1-dichloroacetophenone, 2,2-diethoxyacetophenone, 2,2-dimethoxy-2-phenylacetophenone; thioxanthone series compounds such as 2-chlorothioxanthone, 2-ethylthioxanthone; and compounds such as 2-hydroxy-2-methylpropiophenone, 2-hydroxy-4'-isopropyl-2-methylpropiophenone, 1-hydroxycyclohexylphenylketone, (2-acetyloxy)-1-phenyl-ethanone, methyl $\alpha$-benzeneacetate ($C_6H_5COCO_2CH_3$, sold as NUVOPOL PI 3000, trade name of Rahn Inc. Zurich, Switserland), 2-hydroxy-2-methyl-1-phenyl-propan-1-one which product is marketed by E. Merck, Darmstadt, Germany under the tradename DAROCUR 1173.

The above mentioned photopolymerization initiators may be used alone or as a mixture of two or more.

Examples of suitable photosensitizers are particular aromatic amino compounds as described e.g. in GB-P 1,314,556, 1,486,911, US-P 4,255,513 and merocyanine and carbostyril compounds as described in US-P 4,282,309.

## Optional Additives

The invention is concerned with providing a clear abrasion resistant layer on top of a toner image and therefore, although some pigmentation may be useful, no pigments or dyes are normally incorporated in the radiation curable compositions for use in the present invention. It can be beneficial to add some spacing particles (polymeric beads, $SiO_2$ particles, etc) to the radiation curable composition in order to avoid sticking of the toner images.

It can also be beneficial to include a slip-agent, e.g. silicone slip additives. The abhesive qualities, the flexibility, the abrasion resistance and oxidation resistance of cured layer according to the present invention can be controlled by not only adding a silicone slip additive to the radiation curable composition, but also by mixing a silicon acrylate with the other prepolymers used in the radiation curable composition. Silicone acrylates are formed by the reaction of an organic polysiloxane compound with one or more reactive groups with e.g. an hydroxyacrylate or hydroxymethacrylate.

The invention includes also a method for producing toner images on a substrate comprising the steps of :

i) applying, image wise, toner particles on a substrate forming said toner image,
ii) fixing said toner particles to said substrate, forming an image, and
iii) applying to said image a layer of radiation curable composition in an amount between 1 g/m$^2$ and 20 g/m$^2$ and
iv) radiation curing said composition.

The application of the radiation curable composition and/or the radiation curing thereof can proceed on-line, e.g, the radiation curing proceeds in the fusing (fixing) station itself of an electrostatographic apparatus or in a station immediately adjacent to said fusing station.

The application of the radiation curable composition and radiation curing of it can also proceed off-line in a separate apparatus wherein the fused layer of toner particles and the radiation curable composition on top of it is irradiated with curing rays.

In a further embodiment of this method, between the step of the image wise application of said toner particles on a substrate forming a toner image (step i) and the step of fixing said toner particles to said substrate (step ii) a layer of clear toner particles can be applied over the image.

In a method within the scope of the invention, in step (i) a plurality of layers of different toner particles can be applied to the substrate. The application of a plurality of layers of different types of toner particles (adjacent to each other or superimposed) is beneficial for the formation of full colour images wherein the image is built by the superposition of yellow, magenta, cyan and black toner (YMCK) or in the formation of a black and white (monochrome) image with extended tonal range as disclosed in European Application 95202768, filed on October 13, 1995)

The radiation curable composition can, within the scope of the present invention also be applied on toner images, covered or not with a layer of clear toner particles, before fixing said toner particles and said toner particles are fixed after application of said composition. I.e. in an other embodiment of the method according to the present invention the step of fixing said toner particles is performed after the step of applying a radiation curable composition.

The fixing step in the method described above can beneficially comprise a non-contact fusing step.

The methods, outlined above, are especially suited for the production of full colour images and black and white images wherein the different shades of grey are realized by the superposition of toner particles comprising different amounts of black pigment.

The invention also includes an apparatus for producing toner images comprising :

i) means for image wise depositing toner particles on a substrate,
ii) means for fixing said toner image to said substrate,
iii) means for applying on said toner image a radiation curable composition in an amount between 1 g/m$^2$ and 20 g/m$^2$ of said coating and
iv) means for radiation curing said radiation curable composition.

Since it is preferred, in this invention, to use UV curable compositions the means for radiation curing are UV emitting means (e.g. mercury lamps with giving light with an intensity between 20 W/cm and 150 W/cm.

An apparatus according to the present invention can also comprise, between said means for image wise depositing toner particles on a substrate and means for fixing said toner image, means for applying a layer of clear toner particles, covering the previously applied layer.

Also an apparatus wherein said means for applying said radiation curable composition precede said means for fixing said toner image, is within the scope of the present invention. An apparatus according to this invention and described immediately above, comprises beneficially means for non-contact fusing said toner particles.

Said means for applying said radiation curable composition can be rollers, wicks, sprays, screen printing, offset-printing, gravure rollers, etc. When said means for applying said radiation curable composition are rollers, it may be split rollers, e.g. when 10 g/m$^2$ of radiation curable composition has to be applied, there may be provided four application rollers, the first two applying together 7.5 g/m$^2$ and the following rollers applying the remaining 2.5 g/m$^2$. Preferred means for applying said radiation curable composition are supply rollers with a surface in NOMEX-felt (NOMEX is a trade name of Du Pont de Nemours, Wilmington, US) as described in article titled "Innovative Release Agent Delivery Systems" by R. Bucher et al. in The proceedings of IS&T's Eleventh International Congress on Advances in Non-Impact Printing Technologies, page 219 - 222. This congress was held in Hilton Head, from 29.10.95 to 03.11.95. The proceedings are published by IS&T, Springfield, US 1995. The radiation curable composition can be delivered to the image directly by supply rollers as described above, or over an intermediate roller, which distributes the composition even more evenly over the image.

In a preferred embodiment of an apparatus according to the present invention, said means for fixing said toner particles and said means for UV-curing said UV-curable composition are mounted in said apparatus directly adjacent to each other so that the UV-curing proceeds on the warm curable composition.

When an apparatus according to the present invention comprises in the order given :

i) means for image wise depositing toner particles on a substrate,
ii) means for applying on said toner image a radiation curable composition in an amount between 1 g/m$^2$ and 20 g/m$^2$ of said coating iii) means for fixing said toner image to said substrate and
iv) means for radiation curing said radiation curable composition, it is preferred that said means for fixing are Infra Red (IR) radiators and that both said means for fixing and radiation curing are built together in a single fixing/curing station. This can be done by including a UV-lamp in the fixing station. When the means for applying said radiation curable composition precede the means for fixing the toner image, it is preferred that the application means are non-contact means, e.g. spraying means, an air brush, etc. When spraying means are used to apply the radiation curable composition, the viscosity of said composition is adapted to said spraying. Therefore it is preferred that the viscosity of the radiation curable composition is lower than 3 Pa.s.

The present invention can be practised in any electrographic or magnetographic imaging method. It can be useful in classical electrophotography, in ionography, in direct electrostatic printing (DEP), etc. The present invention is useful for mono-chromatic toner images as well as for multi-chromatic and full colour toner images.
Thus in the apparatus, within the scope of the invention, several means for image wise applying different types of toner particles can be present and said means for image-wise depositing toner particles can be direct electrostatic printing means, wherein charged toner particles are attracted to the substrate by an electrical field and the toner flow modulated by a printhead structure comprising printing apertures and control electrodes. Said means for image-wise depositing toner particles can also be toner depositing means wherein first a latent image is formed. In such an apparatus, within the scope of the present invention, said means for image-wise depositing toner particles) comprise :

- means for producing a latent image on a latent image bearing member,
- means for developing said latent image by the deposition of said toner particles, forming a developed image and
- means for transferring said developed image on said substrate.

Said latent image may be a magnetic latent image that is developed by magnetic toner particles (magnetography) or, preferably, an electrostatic latent image. Such an electrostatic latent image is preferably an electrophotographic latent image and the means for producing a latent image are in this invention preferably light emitting means, e.g., light emitting diodes or lasers and said latent image bearing member comprises preferably a photoconductor.

The present invention can be practised on toner images that are formed with any electrographic imaging method and with any type of toner particles known in the art. The toner particles can be magnetic or non-magnetic. The developer used to form the image can be mono-component magnetic developer, a non-magnetic mono-component developer, a multi-component developer comprising non-magnetic toner particles and magnetic carrier particles.

The toner particles, used to form a toner image according to the present invention can comprise any known toner resin or mixtures thereof. The toner resin can be a polycondensation polymer or a mixture of different polycondensation polymers as well as an addition polymer or a mixture of addition polymers. Also mixtures of polycondensation polymers and addition polymers are suitable as toner resin for toner particles according to the present invention. When polycondensation polymers are used, the use of polyesters is preferred. Polyester resins suitable for use in toner particles according to the present invention are selected e.g. from the group of linear polycondensation products of (i) di-functional organic acids, e.g. maleic acid, fumaric acid, terephthalic acid and isophthalic acid and (ii) di-functional alcohols (diol) such as ethylene glycol, triethylene glycol, an aromatic dihydroxy compound, preferably a bisphenol such as 2,2-bis(4-hydroxyphenyl)-propane called "Bisphenol A" or an alkoxylated bisphenol, e.g. propoxylated bisphenol examples of which are given in US-P 4,331,755. For the preparation of suitable polyester resins reference is made to GB-P 1,373,220. When addition polymers are used, it is preferred to use styrene/acrylic resins. Preferred styrene-acrylic resins have a relatively high (more than 70 mol %) styrene content, and are more particularly copolymers of styrene-acrylic resins or styrene-methacrylic resins, e.g. copoly(styrene/n-butylmethacrylate) or copoly(styrene/2-ethyl-hexylacrylate). Toner particles useful in this invention can have an average volume diameter between 1 and 50 µm, preferably between 3 and 20 µm. When the toner particles are intended for use in colour imaging, it is preferred that the volume average diameter is between 3 and 10 µm, most preferred between 3 and 8 µm. The particle size distribution of said toner particles can be of any type. It is however preferred to have an essentially (some negative or positive skewness can be tolerated, although a positive skewness, giving less smaller particles than an unskewed distribution, is preferred)

Gaussian or normal particle size distribution, either by number or volume, with a coefficient of variability (standard deviation divided by the average) (v) smaller than 0.5, more preferably of 0.3.

The toner particles can comprise any normal toner ingredient e.g. charge control agents, pigments both coloured and black, dyes, release agents, resistivity regulating agents, anorganic fillers, etc. A description a charge control agents, pigments and other additives useful in toner particles, to be used in a toner composition according to the present invention, can be found in e.g. EP-A 601 235.

## EXAMPLES

### 1. Preparation of the toner particles and the developers

#### Yellow toner (Y)

49 parts of a polyester with acid value AV of 17 mg KOH/g (Polyester resin of fumaric acid and DIANOL 33, trade name of AKZO CHEMIE of the Netherlands for bis-propoxylated 2,2-bis(4-hydroxyphenyl)propane) and 49 parts of a polyester with AV of 18 mg KOH/g (Polyester resin of terephthalic acid, isophthalic acid and DIANOL 22, trade name of AKZO CHEMIE of the Netherlands for bis-ethoxylated 2,2-bis(4-hydroxyphenyl)propane, and ethyleneglycol) were melt-blended for 30 minutes at 110 °C in a laboratory kneader with 2 parts of SICOECHTGELB D 1355 DD (Colour Index PY 13, trade name of BASF AG, Germany).

After cooling the solidified mass was pulverized and milled using an ALPINE Fliessbettgegenstrahlmühle type 100AFG (tradename) and further classified using an ALPINE multiplex zig-zag classifier type 100MZR (tradename). The average particle size of the separated toner was measured by Coulter Counter model Multisizer (tradename) was found to be 8.0 µm by volume.

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).

#### Magenta Toner (M)

The preparation of the Yellow toner was repeated, but instead of 2 parts SICOECHTGELB PY13, 2 parts of PERMANENT CARMIN FFB 02 (Colour Index PR146, tradename of Hoechst AG, Germany) were used.

#### Cyan toner (C)

The preparation of the Yellow toner was repeated, but instead of 2 parts SICOECHTGELB PY13, 2 parts of HELIOGEN BLAU D7072DD (Colour Index PB15:3, trade name of BASF AG, Germany) were used.

#### Black toner (K)

The preparation of the Yellow toner was repeated, but instead of 2 parts SICOECHTGELB PY13, 2 parts of CABOT REGAL 400 (carbon black, trade name of the Cabot Corp. High Street 125, Boston, U.S.A.) were used.
The four toners, Y, M, C and K had a meltviscosity at 120 ° C of 250 Pas (measured at a frequency of 16 Hz in a RHEOMETRICS dynamic rheometer, RVEM-200 (One Possumtown Road, Piscataway, NJ 08854 USA). The viscosity measurement is carried out at a sample temperature of 120 °C. The sample having a weight of 0.75 g is applied in the measuring gap (about 1.5 mm) between two parallel plates of 20 mm diameter one of which is oscillating about its vertical axis at 100 rad/sec and amplitude of $10^{-3}$ radians.

#### Developers

Each of the above prepared toners were used to form carrier-toner developers by mixing said mixture of toner particles and colloidal silica in a 4 % ratio with silicone-coated Cu-Zn ferrite carrier particles having an average diameter of 55 µm.

2. UV-curable compositions

Four UV-curable compositions were prepared :

UV1 :

40 g EBECRYL 264 (80 % in HDDA) tradename of UCB, Belgium for an aliphatic urethane acrylate, 10 g HDDA (1,6 hexanedioldiacrylate), 1.5 g of methyl α-benzeneacetate (NUVOPOL PI 3000 trade name of Rahn Inc., Zurich, Switserland and 0.25 g of DC 190 (trade name for a flow additive of DOW chemical, USA) were mixed together.

UV2 :

The composition UV2 Was the same as UV1 except for the amount of EBECRYL 264 and HDDA. In UV2 35 g of EBECRYL 264 and 15 g of HDDA were used.

UV3 :

The composition UV3 was the same as UV1 except for the amount of EBECRYL 264 and HDDA. In UV3 15 g of EBECRYL 264 and 35 g of HDDA were used.

UV4 :

50 g of an alkoxylated tetraacrylate (ATTA) available from Servo Delden BV, Delden, The Netherlands were mixed with 1.5 g of NUVOPOL PI 300 and 0.5 g of DC 190.

3. Printing Example

Full colour toner images were produced using a commercial CHROMAPRESS (a trade name of Agfa-Gevaert NV, Mortsel, Belgium). Off-line all UV-curable coating were applied to the images in different thicknesses. The layers were cured for 0.5 sec by a high pressure mercury lamp with intensity 80 W/cm.
The gloss of the images was measured in a Minolta Multi-gloss 268 reflectometer (trade name of Minolta, Osaka, Japan), the abrasion resistance was measured by manually scratching the image with a stylus with rounded head having a diameter of 0.5 mm and visually evaluating the marks and ranking them from 1 (almost no scratches) to 5 (severe scratching), the solvent resistance against solvents was tested by rubbing the image 10 consecutive times with a cloth soaked with MEK (methylethyleketone) and ranked from 1 (totally resistant) to 5 (all the image away). The results are summarized in table 1. In this table the example without UV cured layer (thickness 0 µm) is a comparative example.

TABLE 1

| Thickness of the layer | Composition # | Gloss | Scratches | Solvent resistance |
|---|---|---|---|---|
| 4 µm | UV1 | < 80 % | 3 | 2 |
|  | UV2 | < 80 % | 2 | 2 |
|  | UV3 | < 80 % | 2 | 2 |
|  | UV4 | > 80 % | 1 | 1 |
| 6 µm | UV1 | < 80 % | 2 | 2 |
|  | UV2 | < 80 % | 1-2 | 2 |
|  | UV3 | > 80 % | 1 | 1 |
|  | UV4 | > 80 % | 1 | 1 |
| 10 µm | UV1 | < 80 % | 2 | 2 |
|  | UV2 | > 80 % | 1 | 1 |
|  | UV3 | > 80 % | 1 | 1 |
|  | UV4 | > 80 % | 1 | 1 |
| 0 µm | - | < 80 % | 3 | 5 |

## Claims

**1.** A toner image fixed on a substrate characterized in that

i) said toner image comprises fused toner particles and
ii) said toner image comprises on top of it a non-image wise applied radiation cured layer, said layer having a thickness between 1 µm and 20 µm.

**2.** A toner image according to claim 1, wherein said radiation cured layer comprises cross-linked compounds and said cross-linked compounds are derived from one or more members selected from the group consisting of unsaturated polyesters, epoxy acrylates, urethane acrylates, polyester acrylates, acrylic acrylates, pentaerythritol tetraacrylate, dipentaneerythritol pentaacrylate, ditriethylolpropane tetraacrylate and alkoxylated tetraacrylate.

**3.** A toner image according to claim 1 or 2, wherein said toner image is a full-colour toner image.

**4.** A method for producing toner images on a substrate comprising, in consecutive order, the steps of :

i) applying, image wise, toner particles on a substrate forming said toner image,
ii) fixing said toner particles to said substrate, forming an image,
iii) applying, on-line or off-line, a layer of radiation curable composition in an amount between 1 g/m$^2$ and 20 g/m$^2$ to said image and
iv) radiation curing said composition.

**5.** A method according to claim 4, wherein the step of fixing said toner particles is performed after the step of applying a radiation curable composition.

**6.** A method according to claim 4 or 5, wherein said radiation curable composition is a UV-curable composition.

**7.** A method according to any of claims 4 to 6, wherein said composition comprises one or more members selected from the group consisting of unsaturated polyesters, epoxy acrylates, urethane acrylates, polyester acrylates, acrylic acrylates, pentaerythritol tetraacrylate, dipentaneerythritol pentaacrylate, ditriethylolpropane tetraacrylate and alkoxylated tetraacrylate.

**8.** An apparatus for producing toner images comprising, in any order :

i) means for image wise depositing toner particles on a substrate,
ii) means for fixing said toner image to said substrate and
iii) means for applying on said toner image a radiation curable composition in an amount between 1 g/m$^2$ and 20 g/m$^2$ of said coating and
iv) means for radiation curing said radiation curable composition.

**9.** An apparatus according to claim 8, wherein said means for applying said radiation curable composition precede said means for fixing said toner particles.

**10.** An apparatus according to claim 9, wherein said means for fixing said toner particles comprise infra-red radiators and said means for curing said radiation curable composition comprise UV-light emitters.

**11.** An apparatus according to claim 9 or 10, wherein said apparatus comprises a fixing/curing station wherein said means for fixing said toner particles and said means for radiation curing are combined.

European Patent
Office

# EUROPEAN SEARCH REPORT

Application Number
EP 96 20 2239

## 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) |
|---|---|---|---|
| X | US-A-4 477 548 (L.P.HARASTA)<br>* column 4, line 1-20; claims 1-34 *<br>* column 16, line 1 - line 4 *<br>* column 17, line 33 - column 18, line 31 *<br>--- | 1-11 | G03G8/00 |
| X | US-A-5 232 812 (I.D.MORRISON)<br>* claims 1-17 *<br>----- | 1,4 | |
| | | | TECHNICAL FIELDS SEARCHED (Int.Cl.6) |
| | | | G03G |

The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| THE HAGUE | 27 January 1997 | Vanhecke, H |

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

&: member of the same patent family, corresponding document