May 30, 1967 E. C. GIAIMO, JR 3,322,537

ELECTROPHOTOGRAPHIC REPRODUCTION PROCESS INCLUDING REMOVAL OF ELECTROSCOPIC PARTICLES FROM DEVELOPED ELECTROSTATIC IMAGE

Filed Nov. 29, 1963

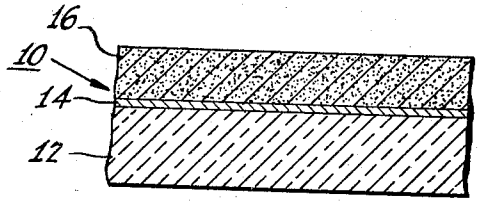


Fig. 1.

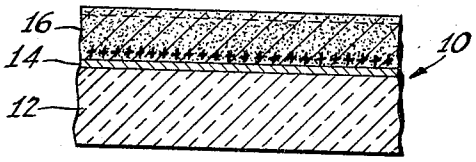


Fig. 2.

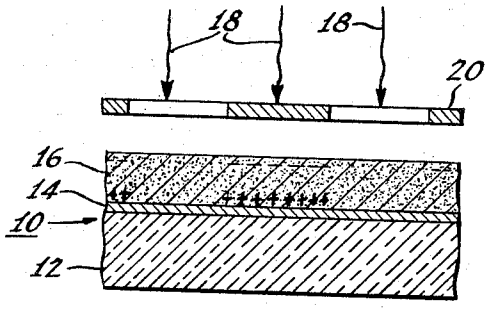


Fig. 3.

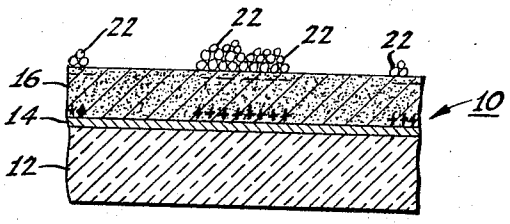


Fig. 4.

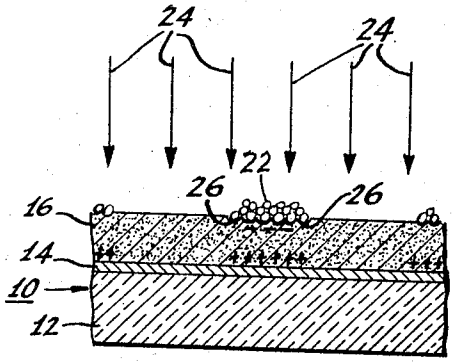


Fig. 5.

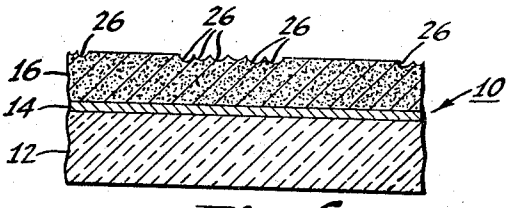


Fig. 6.

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3,322,537
ELECTROPHOTOGRAPHIC REPRODUCTION PROCESS INCLUDING REMOVAL OF ELECTROSCOPIC PARTICLES FROM DEVELOPED ELECTROSTATIC IMAGE

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8 Claims. (Cl. 96—1.1)

This invention relates generally to the art of electrophotographic reproduction, and more particularly to an improved method of developing an electrostatic latent image on an electrophotographic record element. The improved method of the present invention is useful particularly, but not exclusively, for providing information, either temporarily or permanently, on a reusable record element.

It has been proposed to develop an electrostatic latent image on the surface of a record element by a process wherein a toner composed of electroscopic particles is applied to the latent image and the record element is heated to melt or fuse the electroscopic toner into the record element. Such an electrophotographic process is described in an article, "Electrofax," Direct Electrophotographic Printing on Paper, by C. J. Young and H. G. Greig, RCA Review, December 1954, volume XV, No. 4. It has also been proposed to produce a surface-modulated or ripple image of an electrostatic latent image on a thermoplastic layer of a record element by a method wherein the record element is heated to soften the thermoplastic layer, and the electrostatic forces on the softened thermoplastic layer produce the ripple image therein. Such a process is described in an article, Thermoplastic Recording, by W. E. Glenn, Journal of Applied Physics, volume 30, No. 12, December 1959.

While the aforementioned methods of developing images on record elements are suitable for many practical applications, it is sometimes desirable to retain an image on a record element for a relatively short period of time in a manner whereby the image may be viewed either directly or indirectly through an optical system. It may also be desirable to present this information quickly and temporarily in a manner whereby it may be erased easily so that the same record element may be reused to present additional information.

It is an object of the present invention to provide an improved method of developing an image on an electrophotographic record element so that the image may be viewed either directly or indirectly through an optical system.

Another object of the present invention is to provide an improved method of electrophotographic developing wherein a developed image may be erased easily from a record element so that the record element may be reused.

Still another object of the present invention is to provide an improved electrophotographic method of quickly developing an image having a continuous tone rendition.

A further object of the present invention is to provide an improved electrophotographic method of the type described that is relatively easy to apply to known record elements, inexpensive to execute, and highly efficient in use.

Briefly stated, the improved method of developing an electrostatic latent image in accordance with the present invention is practiced in connection with an electrophotographic record element of the type comprising a thermoplastic layer, which preferably, although not necessarily, has photoconductive properties. A toner of electroscopic particles, either in the dry form or suspended in a liquid carrier such as silicone oil, for example, is applied to the thermoplastic layer to render the latent image visible. The melting point of the electroscopic toner particles should be relatively higher than that of the thermoplastic layer. The toned record element is heated to a temperature sufficient to soften the thermoplastic layer but insufficient to melt the electroscopic particles. Under these conditions, depressions or dimples are formed in the thermoplastic layer directly beneath the electroscopic particles, forming a depressed stippled image of the latent image. The developed latent image may now be viewed directly on the record element. If it is desired to project the developed image onto a screen, the electroscopic particles may be removed from the thermoplastic layer by blowing or washing them off, and the remaining dimpled image, having a stippled, frosted-like appearance, may be projected onto a screen with a conventional type optical projector or with a schlieren optical projector. If it is desired to reuse the record element for additional information, the record element may be heated to a temperature to melt the thermoplastic layer so as to smooth it. The record element, when cooled, can then be reused in the manner described in the aforementioned process.

The novel features of the present invention, both as to its organization and method of operation, as well as additional objects and advantages thereof, will be more readily understood from the following description, when read in connection with the accompanying drawing, in which similar reference characters refer to similar parts throughout, and in which:

FIG. 1 is a fragmentary, cross-sectional view of one example of an electrophotographic record element useful in the improved method of the present invention; and

FIGS. 2, 3, 4, 5 and 6 are fragmentary, cross-sectional views of the record element illustrated in FIG. 1 in different stages of the improved electrophotographic developing method of the present invention.

Referring, now, particularly to FIG. 1 of the drawing, there is shown an example of an electrophotographic record element **10** of the type useful in connection with the improved developing method of the present invention. The record element **10** comprises a flexible or rigid substrate **12**, preferably of transparent material, such as "Mylar" or glass, a transparent or reflective conductive coating **14**, such as tin oxide or aluminum, and a thermoplastic layer **16**. The thermoplastic layer **16** may comprise a solid solution of a photoconductor and a thermoplastic resin. Suitable thermoplastic resins in the solid solution of the thermoplastic layer **16** are:

(1) Chlorinated paraffins, such as Chlorowax 70, Diamond Alkali Co., Cleveland, Ohio.
(2) Polyvinylidene chloride.
(3) Polyvinylidene chloride copolymers, such as Saran F–120, The Dow Chemical Company, Midland, Mich.
(4) Polyvinyl chloride.
(5) Vinyl chloride copolymers, such as Vinylite; VAGH, 91% vinyl chloride, 3% vinyl acetate, and 6% vinyl

alcohol; VYCM, 91% vinyl chloride and 9% vinyl acetate; VMCH, 86% vinyl chloride, 13% vinyl acetate, and 1% dibasic acid, Bakelite Division, Union Carbide and Carbon, New York 17, N.Y.

(6) Polystyrene.

(7) Styrene copolymers, such as Piccotex 120, Pennsylvania Industrial Chemical Company, Clairton, Pa.

(8) Butadiene copolymers, such as Pliolite S–5D, Goodyear Tire and Rubber Co., Akron, Ohio.

(9) Polyacrylates, such as Acryloid B–72, Rohm and Haas Co., Philadelphia, Pa.

(10) Acrylic copolymers, such as Lucite 46, E. I. du Pont de Nemours and Co., Wilmington, Del.

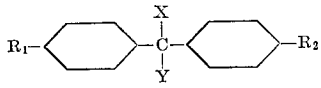
(11) Epoxy resins, such as Epon 1002, Sheel Chemical Company, Houston, Tex.

(12) Thermoplastic hydrocarbon terpene resins, such as Piccolyte S–135, Pennsylvania Industrial Chemical Company.

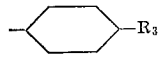
Many advantageous results are also obtainable when combinations of resinous materials are employed, for example, such as:

(13) Compatible mixtures of various resinous materials, such as Acryloid B–72 and Chlorowax.

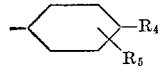
The photoconductor in the solid solution of the thermoplastic layer **16** may be an organic dye intermediate, for example, such as the leucobases of triphenylmethane and benzophenone dyes of the following general formula:



wherein R_1 and R_2 are selected from the class consisting of mono-alkylamino, di-alkylamino, mono-arylamino, and alkylarylamino; X is selected from the class consisting of H, and



wherein R_3 is selected from the class consisting of H, OH, CH_3, OCH_3, and R_1, and



wherein R_4 and R_5 are selected from the class consisting of H, OH, CH_3, and OCH_3; and Y is H except when X+Y is double bonded oxygen.

A photoconductor is not necessary in the thermoplastic layer **16** if the electrostatic latent image is to be produced on the layer **16** by the direct deposition of electric charges, as by directing electrons onto the layer **16** through an apertured stencil.

In carrying out the improved developing method of the present invention, the record element **10** is charged electrostatically by any suitable means known in the art. For example, the layer **16** may be rubbed with silk or fur to deposit a uniform electrostatic charge thereon. The layer **16** may also be charged by corona discharge devices of the type described in the aforementioned article in the RCA Review. The outer surface of the layer **16** may be charged negatively, as shown in FIG. 2, or positively. Where the layer **16** contains a photoconductor, the electrostatic charge is deposited uniformly on the layer **16** in the dark.

An electrostatic latent image can be produced on the layer **16** by selectively discharging the charged layer **16**, as by electromagnetic radiation. For example, the charged layer **16** can be exposed to light, illustrated by arrows **18**, through an apertured stencil, or a photographic transparency **20**, such as a photographic negative or positive, as shown in FIG. 3. The light-struck areas of the layer **16** are discharged in proportion to the amount of electromagnetic radiation, that is, light, impinging on these areas.

The electrostatic latent image may be rendered visible, that is, developed, by applying to the surface of the exposed layer **16** a toner, dry or wet, of electroscopic particles **22**, as shown in FIG. 4. If positively charged toner particles **22** are used, they are attracted to the negatively charged portions of the exposed layer **16** in an amount proportional to the intensity of the electrostatic charges thereon, thus producing a visible image having a continuous tone rendition. The latent image may be developed to provide a visible image that may be considered the negative image of the aforementioned printed image by applying negatively charged electroscopic toner particles **22** to the exposed layer **16**.

Some examples of suitable toners of electroscopic particles useful in the method are:

Example I.—50 grams of polyvinyl chloride-acetate resin, for example, composed of 90% polyvinyl chloride and 10% polyvinyl acetate, and 2 grams of zinc oxide are milled for about 4 hours with quartz pebbles in a small porcelain ball mill. 0.4 part of the milled material are mixed with 100 parts of about 0.015 inch diameter glass beads to form the developer mix, a toner of dry electroscopic particles.

Example II.—200 parts by weight of Piccolastic Resin 4358A (an elastic thermoplastic resin composed of polymers of styrene, substituted styrene and its homologs of the Pennsylvania Industrial Chemical Corp., Clairton, Pa.).

12 parts by weight carbon black.

12 parts by weight Nigrosine SSB—Color Index No. 50415.

8 parts by weight Iosol Black—Color Index Solvent Black 13.

This developer material is prepared by melting the resin and mixing in the other materials. When a uniform mix is obtained, it is cooled, ground to a fine powder and classified to obtain a desired particle size. A convenient particle size is one obtained by screening through a 200 mesh which provides a maximum particle diameter of about 74 microns. This developer material may be dispersed in liquid by any of the commonly known techniques to form a wet toner of electroscopic particles.

Example III.—Toners of colored electroscopic particles, consisting of organic pigments dispersed in dimethyl polysiloxane liquid may be used, prepared as follows: Preferably, the dispersions comprise up to about 20 parts by weight of pigment, the remainder being liquid. The term pigment, as employed herein, is intended to include coloring agents which are sometimes referred to as dyes but which nevertheless are insoluble in the polysiloxane. Suitable pigments for such purposes include the following:

(1) Cyan Blue Toner GT (described in U.S. Patent 2,486,351 to Richard H. Wiswall, Jr.).

(2) Benzidine Yellow (Color Index No. 21090).

(3) Brilliant Oil Blue BMA—Color Index No. 61555.

(4) Sudan 3 Red—Color Index No. 26100.

(5) Oil Yellow 2G—Color Index No. 11020.

(6) Pyrazolone pigment (such as Color Index No. 21080—Color Index Pigment Red 39).

(7) Hansa Yellow G—Color Index No. 11680.

In many of the foregoing dispersions it is convenient to provide a surfactant (surface active agent) to enhance the electrical properties of a selected pigment. A surfactant solution may be prepared by dispersing 10 grams of Nalcamine G–14 in 20 grams of toluene and, while mixing, heating the dispersion to dissolve the Nalcamine G–14 in the toluene. Nalcamine G–14 is a chemical of the type 1-(2-hydroxyethyl) - 2-hydrogenated tallow-2-imidazoline (National Aluminate Corp., Chicago, Ill.). The Nalcamine G–14 solution is added to the pigment dispersions before they are ball milled in the dimethyl polysiloxane. Such a surfactant when applied, for example, to a red pyrazolone pigment substantially enhances the electropositive nature thereof.

The method of developing described herein is applicable to toned "unfixed" images on a thermoplastic layer, regardless of the process of depositing the image of electroscopic particles on the thermoplastic layer. For example, a toned powder image may be transferred to the thermoplastic layer **16** of the record element **10** by any transfer process known in the art. The powder image produced on one surface of a record element by any known prior art method may be transferred to the thermoplastic layer **16** by placing the thermoplastic layer **16** in contact with the powder image and applying a charge of appropriate polarity, as with a corona discharge device, to the thermoplastic layer to attract the electroscopic powder thereto. The transferred powder image on the thermoplastic layer **16** may now be worked upon, as will hereinafter be described.

A toned powder image may also be produced on the thermoplastic layer **16** by first transferring an electrostatic latent image from one record element to the record element **10**. In this method, one record element with an electrostatic latent image thereon is placed against the thermoplastic layer **16** of the record element **10**, and the latent image is transferred to the record element **10** by applying an appropriate charge to the latter of the proper polarity. The electrostatic latent image on the thermoplastic layer **16** may now be rendered visible by applying a suitable toner of electroscopic particles to it.

Where the developed "unfixed" image is of temporary significance, it may be viewed in the form illustrated in FIG. 4 of the drawing.

It is sometimes desirable to use a relatively small record element **10** and to enlarge the developed image thereon, as by projecting the image onto a screen through an optical system. For this purpose, the record element **10** with its visible image of toner particles **22** is heated, either on a hot plate, or by radiant heat, or by a stream of hot gas, illustrated by arrows **24**, to a temperature at which only the thermoplastic layer **16** softens. The electroscopic toner particles **22** should have a relatively higher melting point than the thermoplastic layer **16**. Accordingly, the layer **16** should be heated to a temperature sufficient to soften it only, but insufficient to soften the toner particles **22**. Under these conditions, depressions or dimples **26** are formed in the surface of the layer **16** directly beneath the toner particles **22**, as shown in FIG. 5. The dimples **26** provide a stippled, frosted-like visible image of the electrostatic latent image. The record element **10**, as shown in FIG. 5, may now be viewed through any suitable optical system (not shown) since the substrate **12**, the conductive coating **14**, and the thermoplastic layer **16** are transparent, except for the developed image.

Suitable record elements for practicing the improved developing method of the present invention may be prepared in accordance with the following examples:

Example A

A thermoplastic layer for the record element consists of the following ingredients:

21% by weight bis(4,4' - dimethylaminophenyl) - phenyl methane 4,4' - [benzylidene - bis(N,N - dimethylamine)], and

79% by weight sucrose-benzoate ($C_{12}H_{22}O_{11}$ esterified to 90% with benzoic acid, resulting in 7.2 out of 8.0 possible hydroxyls being a non-crystalline, hard glossy solid) having an average molecular weight of 1110 and a softening range around 90–93° C. Manufactured by Tennessee Products and Chemical Corp., Nashville, Tenn.

The aforementioned ingredients are mixed and heated to about 120° C. to form a solution that is applied to a suitable substrate, such as, for example, a conductive glass or a metallized transparent plastic. A preferred substrate is lantern slide glass having on one surface thereof a vacuum deposited conductive film such as, for example, tin chloride. When cooled, the thermoplastic layer of the record element has a melting point in the neighborhood of 90–100° C.

Example B

The following ingredients for a thermoplastic layer of a record element are combined by weight percent:

31.4% bis(4,4' - dimethylaminophenyl)-2-hydroxyphenol methane 4,4' - [2 - hydroxybenzylidene - bis(N,N - dimethylaniline)],

67.2% sucrose benzoate, and

1.4% Vinylite VAGH, a copolymer of 81% vinyl chloride, 3% vinyl acetate, and 6% vinyl alcohol made by Bakelite Division of Union Carbide and Carbon, New York 17, N.Y.

The above ingredients, constituting the composition of the desired solid solution of the thermoplastic layer, are dissolved in a solvent consisting of 21% methyl ethyl ketone and 32% toluene, the percent of the solvents being in weight percent of the total composition. The solution is applied to the surface of a glass lantern slide metallized with tin chloride and dried by gentle heating at about 40° C. When cooled, the resulting thermoplastic layer has a melting point at around 70° C.

Example C

A thermoplastic layer comprises the following ingredients by weight percent:

33.2% bis(4,4'-dimethylaminophenyl)-phenyl methane 4,4'-[benzylidene-bis(N,N-diethylaniline)],

65.5% sucrose benzoate, and

1.3% Vinylite VAGH.

When these ingredients are thoroughly mixed, 48% by weight of the mixture is mixed with 20% by weight of methyl ethyl ketone and 32% by weight of toluene, the percent weight of the solvents being in weight percent of the total composition. The materials of the thermoplastic layer are dissolved in the solvent and the solution is applied to the metallized coating (tin chloride) on a glass lantern slide as by roll coating, flow coating, or dipping. When the thermoplastic layer is dried, it has a melting point in the neighborhood of 70° C.

If desired, the electroscopic toner particles **22** may be removed as by blowing them or by washing them off the layer **16**, leaving a depressed stippled image of the latent image, as shown in FIG. 6. The removal of the toner particles may be aided by discharging the thermoplastic layer **16** completely, as by exposing it to bright light. The stippled image may be projected upon a screen by either a conventional or a schlieren optical system. The record element **10** may also be stored in this condition, the stippled image providing a permanent record. Where this record is merely of temporary importance, the dimpled image may be removed from the layer **16** by applying heat to the layer **16** of an intensity sufficient to melt it so as to smooth it, thereby to erase the dimpled image thereon. Thus, the record element **10** may be reused in the manner heretofore described.

The record element **10** with its depressed stippled image formed by the dimples **26** may be used as a printing plate in an intaglio printing press. When engraving ink is deposited in the depressed stippled image, the ink may be transferred to a sheet of paper by pressing the record element **10** against the paper sheet.

From the foregoing description, it will be apparent that there has been provided an improved method of printing information on an electrophotographic record element in a manner whereby the information may be retained permanently or temporarily, and also in a manner whereby the printed image may be viewed directly or indirectly through an optical system. It is also apparent that the improved method of the present invention provides an economical use of record elements in that the record ele-

ments may be reused repeatedly and the electroscopic toner particles may be reclaimed. While only a limited number of examples of applications of the improved printing method of the present invention have been described, variations coming within the spirit of this invention will, no doubt, readily suggest themselves to those skilled in the art. Hence, it is desired that the foregoing shall be considered as illustrative and not in a limiting sense.

What is claimed is:

1. A method of producing an image, said method comprising the sequential steps of

(a) charging a thermoplastic photoconductive layer with an electrostatic charge,

(b) exposing said charged layer to an image of electromagnetic radiation to discharge said layer selectively, whereby to produce an electrostatic latent image thereon,

(c) adding a toner comprising electroscopic particles to said exposed layer to render said latent image visible, the softening temperature of said particles being higher than the softening temperature of said layer,

(d) applying heat to said layer to soften said layer only, said heat being of a temperature sufficient to soften said layer but insufficient to melt said particles, whereby depressions are formed in said layer beneath said particles, and

(e) removing said particles from said layer, whereby to leave an image comprising depressions in said layer.

2. A method of producing an image comprising a plurality of depressions in a thermoplastic photoconductive layer of a record element, said method comprising the sequential steps of

(a) charging said layer with a uniform electrostatic charge,

(b) exposing said charged layer to a light image to discharge said layer selectively, whereby to form an electrostatic latent image thereon,

(c) adding a toner comprising electroscopic particles to said exposed layer to render said latent image visible, the softening temperature of said particles being higher than the softening temperature of said layer,

(d) directing a stream of hot gas onto said layer to soften said layer only, said stream of hot gas being of a temperature sufficient to soften said layer but insufficient to melt said toner, whereby said depressions are formed in said layer beneath said particles, and

(e) removing said particles from said layer, whereby to leave said image comprising said depressions in said layer.

3. A method of producing an image comprising a plurality of dimples in a thermoplastic photoconductive layer of a record element, said method comprising the sequential steps of

(a) exposing said layer to an image of electromagnetic radiation to charge the conductivity of said layer selectively,

(b) charging said layer with an electrostatic charge to produce thereon an electrostatic latent image of said image of electromagnetic radiation,

(c) adding a toner comprising electroscopic particles to said exposed and charged layer to render said latent image thereon visible, the softening temperature of said particles being higher than the softening temperature of said layer,

(d) applying heat to said layer to soften said layer only, said heat being of a temperature sufficient to soften said layer but insufficient to melt said toner, whereby said plurality of dimples are formed in said layer beneath said toner particles,

(e) removing said particles from said layer, whereby to leave said image comprising said dimples in said layer, and

(f) heating said layer sufficiently to cause said dimples to disappear, whereby said record element may be reused.

4. In an electrophotographic method wherein an electrostatic latent image is produced on a thermoplastic layer of a record element, the improvement comprising the sequential steps of

(a) adding a toner comprising electroscopic particles to said layer to render said latent image visible, said toner having a melting point that is higher than that of said layer,

(b) applying heat to said layer, said heat being of an intensity sufficient to soften said layer but insufficient to soften said particles, whereby to form depressions in said layer directly beneath said particles, and

(c) removing said particles from said layer, whereby to leave an image comprising said depressions in said layer.

5. In an electrophotographic method wherein an electrostatic latent image is produced on a thermoplastic layer of a record element, the improvement comprising the sequential steps of

(a) adding a toner comprising electroscopic particles to said layer to render said latent image visible, said toner having a softening temperature higher than that of said layer,

(b) directing a stream of hot gas onto said layer, said stream of hot gas having a temperature sufficient to soften said layer but insufficient to soften said particles, whereby to form dimples in said layer directly beneath said particles,

(c) removing said particles from said layer, whereby to leave an image comprising said dimples therein, and

(d) heating said layer to a temperature sufficient to melt said layer, whereby to remove said dimples and to smooth said layer so that it may be reused when desired.

6. In an electrophotographic method of the type wherein an image of electroscopic particles is produced on a thermoplastic layer of a record element, and wherein said particles have a higher melting point than said layer, the improvement comprising the sequential steps of

(a) applying heat of a predetermined temperature, said predetermined temperature being sufficient to soften only said layer but insufficient to soften said particles, whereby to form depressions in said layer directly beneath said particles, and

(b) removing said particles from said layer.

7. In an electrophotographic method of the type wherein an image of electroscopic toner particles is produced on a thermoplastic layer of a record element, the improvement comprising the sequential steps of

(a) directing a stream of heated gas onto said layer, said particles having a higher melting point than said layer, and said stream of heated gas having a temperature sufficient to soften said layer but insufficient to soften said particles whereby to form dimples in said layer directly beneath said particles,

(b) cooling said layer, and

(c) removing said particles from said cooled layer, whereby to leave an image comprising said dimples in said layer.

8. In an electrophotographic method of the type wherein an image of electroscopic toner particles is produced on a thermoplastic layer of a record element, the improvement comprising the sequential steps of

(a) heating said layer, said particles having a higher melting point than said layer, said heat having a temperature sufficient to soften said layer but insufficient to soften said particles, whereby to form dimples in said layer directly beneath said particles, and

(b) cooling said layer,

(c) removing said particles from said cooled layer, whereby to leave an image comprising said dimples in said layer, and

(d) reheating said layer to smooth the surface of said layer, whereby said record element may be reused.

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