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(54) Improved method for providing permanent images.

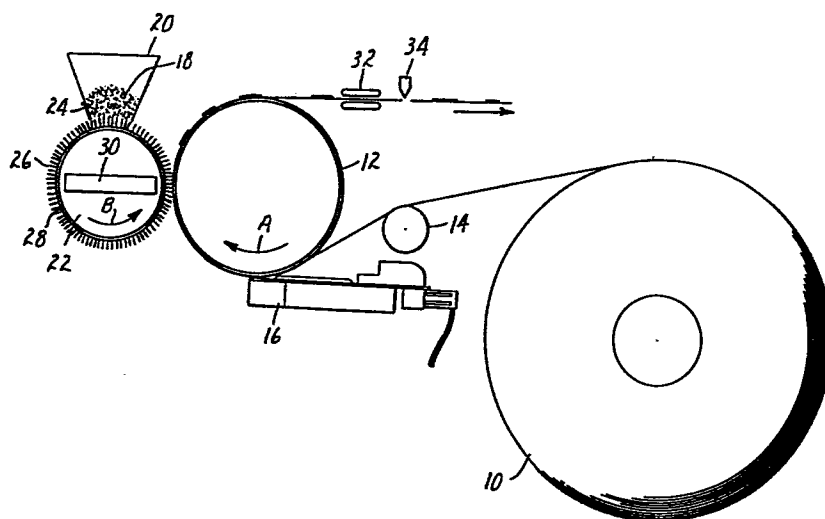
(57) This invention relates to image generation by thermal printing means.

Thermal printing means, such as a thermal print head, are employed to raise the temperature of a normally solid, non-tacky material above its melting temperature and provide a latent liquid image area on heat-sensitive substrate. The latent liquid image can then be developed with a dry imaging powder. In a subsequent step, the developed image can be fixed by means of pressure. In the two-step developing/fixing sequence, the substrate bearing the developed image passes through squeeze rolls to fix the image. Sophisticated, expensive steering mechanisms must be used with the squeeze rolls to guide the substrate smoothly through the rolls to prevent the formation of wrinkles and creases in the substrate.

The present invention is directed to a process whereby the image areas of the substrate are simultaneously developed and fixed by contacting them, under sufficient pressure, with a dry magnetizable imaging powder that becomes permanently attached thereto. The one-step developing/fixing procedure eliminates the employment of sophisticated steering mechanisms. The process is useful wherever it is desired to generate images from electronic data sources such as computers, facsimile transceivers, chart recorders, teleprinters, etc., and provide such images in essentially permanent form.

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IMPROVED METHOD FOR PROVIDING PERMANENT IMAGES

Background of the Invention

This invention is related to image generation.

5 More particularly it is related to techniques wherein a thermal printing means is employed to form latent images on a substrate, which image is subsequently developed with a dry imaging powder and fixed by means of pressure. The developing step and fixing step are conducted
10 simultaneously.

Image generation processes utilizing heat are known and are often referred to as thermographic processes. They generally require image-wise exposure of a heat-sensitive material to heat. This may cause a chemical
15 reaction of the heat-sensitive material thereby producing a visible image. Alternatively, it may cause the heat-sensitive material to become either tacky or fluid in exposed areas. In either event, the tacky or fluid image may then be developed with an imaging powder.

20 Examples of thermographic recording processes are set forth in United States Patents 3,196,029; 3,260,612; 3,515,570; and 3,941,596. These patents disclose processes wherein a substrate having a layer of a heat-sensitive material is imaged by use of a master or an original
25 document. The image may then be toned with a powder or dye.

In U. S. Patent 3,196,029, an original document is placed on the heat-sensitive layer. The original is then exposed to infra-red radiation. The image areas of
30 the original absorb the radiant energy and heat up causing the heat-sensitive layer to soften and produce a latent image. The image is then made visible by contact with a powder. The powder may then be fixed by either heating it or exposing it to solvent vapor. However, fixing is
35 optional.

In U. S. Patent 3,260,612, an image is formed by placing an original document on the heat-sensitive layer of

a substrate and exposing the original to infra-red radiation. The image is made visible by contact with a powder or a dye.

5 In U. S. Patent 3,515,570, the heat-sensitive layer comprises a first material which shows a stable supercooling property and has a melting point of 45°C to 120°C, and fine particles of a second material which does not show the supercooling property and has a melting point at least 10°C higher than the melting point of the first material.
10 Images are formed as described above.

In U. S. Patent 3,941,596, a heat-sensitive material of a mixture of a thermoplastic, amorphous, organic polymer and a liquid plasticizer, is utilized. After image formation, the image is made visible by either
15 contact with a toner powder or by transfer of the image to a receptor followed by contact with a toner powder.

Each of these processes requires the use of a graphic original or graphic master and sophisticated equipment and, frequently, the use of special coated or
20 treated papers. Moreover, the heat generated during some of these processes is great, thereby necessitating the use of cooling equipment such as fans in order to give acceptable machine life to the equipment. Additionally, the heat of the process may cause formation of noxious gases which
25 are released to the area surrounding the equipment and can make these areas very uncomfortable and offensive for operators during periods of high usage.

The heat required to fix the images, such as in U. S. Patent 3,196,029, is disadvantageous for other
30 reasons. It limits the speed of the recording process and the substrates that can be used. Still further, the heat requires a significant degree of power consumption and, as noted above, liberates a significant amount of heat which may render the surrounding environment uncomfortable.

35 The invention disclosed in Wartman, U.S. Application 241,766, filed March 9, 1981, eliminates the need for a graphic original or master by relying on the

generation of an electronic signal which activates a thermal printing means for generating a heat pattern or a receptor to give a latent image which can be powder developed. It provides a simple, quiet, clean, cool, and economical process for providing permanent images on a substrate. Moreover, the invention in Wartman, U.S. Application 241,766, provides an instant-on system. Thus, no warm-up time is needed and no steady supply of heat must be provided between periods of use. The advantage of the present invention over that disclosed in U.S. Application 241,766 is that the present invention further provides a process for simultaneously developing and fixing the colored powder image. This simultaneous developing and fixing process has several advantages over the process where development and fixing are sequential.

In the sequential process, the substrate with the developed image passes through squeeze rolls to fix the image. Sophisticated, and consequently, expensive steering mechanisms must be used with the squeeze rolls to guide the substrate smoothly through the rolls to prevent the formation of wrinkles and creases. In the simultaneous process of the present invention, the squeeze rolls and accompanying steering mechanism are eliminated. There is no tendency for wrinkles and creases to form because the substrate does not have to be guided into an image fixing mechanism separate from the image development mechanism.

The squeeze rolls used in the sequential process may weigh about 10 to 20 pounds or more for an 8-1/2 inch wide substrate, and may occupy a volume of about 75 cubic inches or more. In contrast, the developing and fixing mechanism in the simultaneous process weighs only about two pounds and occupies only about 10% of the volume of the sequential process. The lower weight and volume is particularly critical where the portability of a printing machine is important.

The simultaneous process reduces the time required to obtain a readable image from a latent image by

at least about 50% over the sequential process. For example, if the substrate passes at a rate of one inch per second over a stationary thermal print head and the distance to the developing fixing mechanism of the simultaneous process is two inches, a fixed, visible image will be developed in two seconds. By comparison, if, in the sequential process, the distance to the developing mechanism is two inches and the distance to the squeeze rolls is an additional three inches, a fixed visible image will be produced in five seconds.

Summary of the Invention

In accordance with one aspect of the present invention there is provided a method for providing a permanent image upon a substrate wherein the image is a dry magnetizable imaging powder, wherein fixing is achieved by the application of pressure applied simultaneously with the developing by the imaging powder. The method comprises the steps of:

providing a substrate bearing a coating of a normally solid, non-tacky material which has a melting temperature at least 10°C above ambient (typically above about 45°C) and forms a supercooled melt when cooled to a temperature below its melting temperature;

forming a latent image pattern on said coating by image-wise contacting said coating to a thermal printing means for a time sufficient to raise the temperature of said non-tacky material to at least its melting temperature;

contacting said latent image pattern with a dry colored magnetizable powder under sufficient pressure to attach and embed the colored magnetizable powder to said latent image pattern, and form a substantially unified and visually continuous mass thereon.

As it is used herein, the term "latent liquid image" means a fluid image that is generally not readily perceptible to the naked eye as an image. Such images are

provided by image-wise heating the coated surface of the substrate to a temperature sufficient to melt the non-tacky material.

5 The latent liquid image areas need only be macroscopically (that is, visually) continuous. Thus, even though they appear to be continuous when examined by the naked eye, they need not be. They may comprise halftone dots or other forms of discontinuous liquid areas which generally make up the graphic character to be reproduced.

10 The process of the invention calls for simultaneous application of imaging powder to the latent image and fixing of the permanent image. This process is desirable because it makes feasible a reduced size, reduced weight, low cost printer which provides a visible, readable
15 image in a very short interval after an electronic signal is received by the thermal print head.

20 Additionally, the amount of energy required to achieve suitable fixing, and the amount of heat generated during fixing are substantially reduced. This not only dramatically reduces heat build-up in the machine and the area surrounding it, but also avoids problems associated with heating and tackifying the entire sheet. Such total heating and tackifying renders the background areas of the sheet susceptible to smearing. Additionally, it creates
25 problems of image offsetting, image smearing, and finger-printing until the coating or particles on the sheet recrystallize.

30 The process of the present invention is also quiet. Consequently, it is not a distracting influence to those compelled to work in the area of process. Still further, the process does not require the use of sophisticated machinery, such as electrophotographic imaging equipment. Consequently it is simple and economical to employ.

35 Brief Description of Drawing

The Figure is a schematic view of the apparatus of the present invention.

Detailed Description of the Invention

The process of the present invention is easily carried out. It comprises the steps of providing a defined substrate, forming a latent liquid image thereon, simultaneously contacting the liquid image with a magnetizable toner powder and fixing the image thus formed with pressure to provide a unified, essentially permanent image on the substrate.

The substrate used in the invention may be selected from any dry, solid material which is compatible with the coating of normally solid, non-tacky material. Examples of such materials include polymeric films, metal foils, and paper. Most preferably the substrate is paper.

The substrate preferably bears from about 0.5 to about 5 g/m² of the coating material attached to its surface. The coating material may be applied to the surface of a substrate by a variety of techniques including solvent coating and dry coating. For example, the selected normally solid, non-tacky material may be dissolved or dispersed in an appropriate solvent (e.g., acetone, or water), the solution or dispersion applied to the substrate, and the solvent allowed to evaporate. The dissolved solid material is allowed to crystallize. Evaporation of the solvent may be accelerated, if desired, by heating the coated substrate. However, care should be taken to insure that the substrate does not curl or otherwise suffer adverse effects as a result of the heating. Additionally, crystallization of the dissolved solid material may be accelerated by seeding the coated substrate with undissolved solid material.

Thickening agents may be added to the coating solutions and dispersions, if desired, to improve their handleability or coatability. Typically only a small amount of such agents is required, e.g., 20% by weight or less of the coating solution. These materials are known and include, for example, ethyl cellulose and styrene/acrylic acid/ethylacrylate terpolymer.

Dry coating techniques may also be utilized. Thus, one may brush or rub the solid form of the non-tacky material onto the substrate. Preferably the material, when applied to the substrate, is either a powder or a form in which it may readily be converted to a powder. This dry coating technique provides an efficient means for applying the material to the substrate. Thus, materials applied by the dry coating technique do not soak into the substrate as they do with solvent coating techniques. Furthermore, when a plain paper substrate is coated by the dry coating technique, the resultant sheet appears indistinguishable from an uncoated paper sheet and can be used immediately after coating.

The exact amount of the solid material applied to the substrate is not critical to the invention, provided that there is sufficient material to form a latent image and not so much material that it fouls the thermal printing means, becomes too dielectric, or gives a greasy feel or appearance to the substrate. Additionally, a sufficient amount of the material must be used so that once the latent image has been formed, there will be sufficient adhesion between it and the imaging powder to overcome both the triboelectric and magnetic forces holding the imaging powder to the development roll.

It has been found that a small quantity of the coating material is all that is needed to provide these results. Thus, it has been found that from about 0.5 to about 5 g/m² provides excellent results. When solvent coating is utilized, the substrate preferably bears from 1.0 to 4.0 g/m² of the material, and more preferably from about 2.0 to 3.5 g/m² of the material. Surprisingly these small quantities of material are sufficient to provide latent images that can be developed and essentially permanently fixed to the substrate.

When dry coating techniques are employed, the particulate material is substantially absorbed onto the substrate surface. Thus, for example, when the substrate

is paper, the material becomes attached to the surface of the paper fibers.

5 The material utilized as the solid, non-tacky, material of the coating must have a melting temperature about 10°C above ambient temperature. Ambient temperature, as used herein, refers to the temperature utilized during the process. The coating must also form a supercooled melt when cooled to a temperature below its melting temperature. These materials may be said to exist, at least temporarily, 10 as fluid metastable liquids after being melted then cooled below their melt temperatures. When the latent image has been formed, it should wet the surface of the substrate. Moreover, the image must remain fluid and in place until it is contacted with (that is, developed by) the dry imaging 15 powder. Alternatively, it may be allowed to cool below its melting point to form a supercooled melt before the image areas are developed. At this point the supercooled liquid has not regained its solid crystalline state. Consequently, the material retains sufficient memory in the imaged areas 20 to be developed and fixed. Once the material regains its crystalline state in the imaged areas, the latent image ceases to exist as a distinct area.

The imaged area must also adhere the dry imaging powder. Thus, for example, the imaged area may react with 25 the imaging powder; it may form a solution with the powder; it may wet the powder; or it may either absorb or be absorbed by the powder.

A number of materials are useful as the coating in the invention. Representative examples of these materials 30 include dicyclohexyl phthalate, diphenyl phthalate, triphenyl phosphate, dimethyl fumarate, benzotriazole, 2,4-dihydroxy benzophenone, benzophenone, and benzil. Another useful material of this type is "Santicizer 9", a mixture of ortho- and para-toluene sulfonamides obtained 35 from the Monsanto Chemical Company.

A variety of imaging powders are useful in the present invention. The imaging powder comprises a colored

magnetizable powder having a particle size ranging from about 1 micron to about 40 microns, as required for fixing, edge definition, and resolution. Useful dry powders may be similar to commercial heat fixing or pressure fixing dry powders currently used in the copying industry. A useful powder of the heat fixing type comprises the following ingredients in the amounts indicated:

Bisphenol A fumarate	40-45 percent by weight
Magnetite	55-60 percent by weight
Carbon	1-2 percent by weight

The preferred toner powders are neither of the heat fixing type nor of the pressure fixing type. They are insensitive to heat and/or pressure. Useful powders in this category include iron (reduced electrolytic, 1X 250, manufactured by Matheson, Coleman, and Bell, Norwood, Ohio having a particle size range of 3 to 30 microns and an average size of 10 microns) and nickel (Type 287 manufactured by International Nickel Co., New York, N. Y. having a particle size of 2.6 to 3.3 microns).

Other useful powders must be magnetizable and are preferably heat and pressure insensitive. Useful powders include cobalt, chromium oxide (CrO_2), magnetite (Fe_3O_4), cobalt doped magnetite, $\gamma\text{-Fe}_2\text{O}_3$, an alloy comprising 39 percent cobalt and 57 percent iron, and an alloy comprising 10.6 percent nickel and 79 percent iron.

In the process of the invention a latent image pattern is first formed on the coated substrate. Any thermal printing means, such as a hot stylus, a jet of hot air, a thermal print head, or a laser may be used to provide the latent image.

In one embodiment of the invention the latent image comprises a series of melted dot-like areas on the coating. These areas may be provided by any of the techniques described above, although the following description refers to the use of a thermal print head.

Thermal print heads are known. In the simplest sense they comprise at least one resistance element between

two conductors. The thermal print head may also comprise an array of resistance elements. Thus, for example, there may be a 5 by 7 element array on the print head. Additionally, the print head may be fixed or moveable with respect to the surface to be imaged.

The latent image pattern is formed by contacting the resistance element to the coating, providing electric current to the element for a time sufficient to heat the element and raise its temperature to a level sufficient to melt the coating in the area of contact, discontinuing the electric current to the element, and relocating the element on the coating. The steps of contacting, heating and relocating are repeated until a sufficient number of melted dot-like areas have been provided to define the desired latent liquid image.

When the print head has only a single element, or set of elements, the steps necessary to form the latent image must be repeated frequently before an image has been defined. When the print head comprises an array (or matrix) of elements, the steps necessary to form the latent image formation need be repeated fewer times. The print head receives an electrical signal that is converted to heat for an appropriate length of time and at the appropriate location on the substrate.

After formation of the latent image, the imaging powder is applied and fixed simultaneously. Preferably a rotating magnetic developer roll having a brush applicator attracts the imaging powder to its surface and transports it to the image area where the powder is then attached to the image area but not to the background area. The pressure required to fix the image is approximately 5 to 300 g/cm², depending upon the type of imaging powder used, the nature of the coating, or the nature of the substrate.

The developing-fixing assembly contains a permanent magnet, a brush applicator, a toner (imaging powder) dispenser, and a means for applying pressure between the brush applicator and print paper. An example

of a suitable permanent magnet is designated by the trademark Alnico 5 and is manufactured by Arnold Engineering Co., Chicago, Illinois. An example of a suitable brush applicator is designated by the trademark Cotton Velvet "Brittany Beige" and is manufactured by the J. B. Martin Co., Leesville, South Carolina.

Referring now to the figure, a roll of the coated paper 10 is brought into contact with drum 12 by means of idler roll 14. It is contemplated that the drum 12 is driven at a surface speed of about one inch per second in the direction of the arrow A. However, the speed is not a critical aspect of the invention, and higher speeds or lower speeds may be utilized. The paper is contacted by a thermal print head 16 which produces a latent image on the paper 10.

A reservoir of magnetizable powder 18 is contained in hopper 20 and is metered to the brush applicator 22 by gate 24. The brush applicator 22 comprises a cotton velvet material 26 wrapped around hollow aluminum roll 28 which rotates in the direction of the arrow B at about four revolutions per second. Here again, the speed is not a critical aspect of the invention. However, it should be noted that the speed of the aluminum roll 28 must be compatible with the surface speed of the drum 12. The magnetizable powder 18 becomes embedded in the nap of the brush applicator 22. The magnetizable powder 18 is attracted to permanent magnet 30 and will not transfer to areas of paper 10 that do not have a latent image pattern. This has the beneficial result of improving edge definition and resolution. Areas of paper 10 that have a latent image pattern are tacky and have an adhesive force strong enough to overcome the magnetic force and cause transfer of the colored powder 18 to the latent image pattern. A pressure of 40 g/cm^2 between roll 28 and paper 10 during transfer can be obtained by means of springs (not shown) attached between aluminum roll 28 and drum 12. The pressure aids in forcing the powder into the latent image pattern to produce

a fixed image which cannot be easily removed, even by vigorous rubbing with a finger. The imaged paper 10 is transported through slot 32. After the desired amount of print has been made, the paper 10 is manually torn off using knife 34.

The substrate employed in the process of the invention may be chosen from a variety of materials. Preferably it is thin and flexible and may be transparent or opaque. Thus, the substrate may be selected from, for example, paper, polymeric films such as polyesters, cellulose triacetate, polypropylene, etc. The high thermal conductivity of metals renders such materials as aluminum and copper less attractive than substances having low thermal conductivity.

The present invention is illustrated by the following examples. These examples are not to be construed as limitative.

Example I

A sheet of machine finished paper (37 lb. per 3000 square feet) was coated with a solution comprising 24% by weight dicyclohexylphthalate (DCHP), 5% by weight ethyl cellulose (Hercules, Incorporated N-200) and 71% by weight acetone.

The coated paper was dried by allowing the acetone to evaporate for about 10 minutes into a room at normal temperature and humidity to provide a dried coating weight of 2.7 g/m^2 . The dried coated substrate was aged for one week to insure that the DCHP was in a crystalline state. The crystallization process may be accelerated by seeding the coated substrate with dry DCHP. The dried coated paper was then cut into strips.

Latent liquid image areas were provided on one strip of the dry coated paper by passing it through a Texas Instrument Model TI5040 electronic printing calculator. This calculator heated the imaged areas of the paper to about 85°C . The latent liquid image areas were then rubbed

with iron powder which had been embedded in the nap of velvet material which had been wrapped around a magnet. The iron powder, manufactured by Matheson, Coleman and Ball of Norwood, Ohio, had a particle size range of 3 to 30
5 microns. The velvet material, manufactured by J.B. Martin & Co., Leesville, S.C., was designated Cotton Velvet, "Brittany Beige". The nap was estimated to be 1/16 inch long. The magnet, manufactured by Arnold Engineering Co., Chicago, Ill., was a bar magnet designated "Alnico 5".

0 The rubbing was conducted on the pan of a trip balance in such a way that the balance was in equilibrium.

Prints having good image adhesion were obtained over pressures ranging from 10 g/cm² to 360 g/cm². At the higher pressure, a slight tendency towards backgrounding
5 was observed.

Example II

This Example was identical to Example I, with the exception that nickel powder, Type 287, manufactured by
10 International Nickel Company, New York, N.Y. was substituted for the iron. The nickel powder had a particle size range of 2.6 to 3.3 microns.

A print having good image adhesion was obtained at a pressure of 40 g/cm².

Example III

A sheet of Substance 12 "Mirraform" paper manufactured by the Nekoosa Edwards Paper Company was coated with a solution comprising 24% by weight diphenyl
30 phthalate (DPP), 5% by weight ethyl cellulose (N-200 from Hercules, Incorporated) and 71% by weight acetone. The coating was dried as described in Example 1 to provide a dried coating weight of 2.7 g/m². The sheet was then aged for over one week to insure all the DPP was in the
35 crystalline state. The dried sheet was cut into individual strips.

One of the strips of the dry coated paper of this example was imaged, toned, and fixed according to the procedures, and with the toner powder, described in Example II. Sharp, permanently bonded dark grey images on white paper were obtained. The images could not be removed by rubbing them with a finger.

Example IV

This Example was identical to Example I, with the exception that the dicyclohexyl phthalate coating was applied to super calendered "3M Dry Silver" base stock (39 lb. per 3000 square feet) manufactured by Simpson Paper Co., San Francisco, California. The toner had the following composition:

Bisphenol A fumarate	40-45 percent by weight
Magnetite	55-60 percent by weight
Carbon	1-2 percent by weight

The particle size of the toner was 8-20 microns. A print was made at a pressure of 20 g/cm², yielding an intense black image on a white background. The image could not be removed by rubbing with a finger.

Example V

Triphenyl phosphate was pulverized to a powder and then rubbed on the paper of Example I by means of a cotton pad. In this manner, a continuous, adherent coating was obtained.

The dry coated paper was printed in the Texas Instrument Model TI 5040 and rubbed with the iron powder of Example I. An adherent gray-colored image on a white background was obtained. The image was not removed when rubbed with a finger.

CLAIMS:

1. The method of providing a permanent image on a substrate comprising the steps of:

5 providing a substrate bearing a coating of a normally solid, non-tacky material which has a melting temperature at least 10°C above ambient and which forms a supercooled melt when cooled to a temperature below its melting temperature;

10 forming a latent image pattern on said coating by generating an electric signal to activate a thermal printing means and image-wise contacting said coating with the thermal printing means for a time sufficient to raise the temperature of said non-tacky material to at least its melting temperature;

15 simultaneously contacting said latent image pattern with a dry imaging powder which attaches to said latent image pattern and applying sufficient pressure to said imaging powder to fix the powder image and form a permanent image thereon.

2. The method according to claim 1 wherein said coating is provided on said substrate by applying said normally solid, non-tacky material thereto immediately prior to forming said latent image pattern thereon.

3. The method according to claim 1 wherein said non-tacky material is selected from dicyclohexyl phthalate, diphenyl phthalate, triphenyl phosphate, dimethyl fumarate, benzotriazole, 2,4-dihydroxy benzophenone, benzophenone, and a mixture of ortho- and para-toluene sulfonamides.

4. The method according to claim 3 wherein said solid material is dicyclohexyl phthalate.

5. The method according to claim 3 wherein said solid material is triphenyl phosphate.

6. The method according to claim 3 wherein said solid material comprises a solid solution of dicyclohexylphthalate and diphenylphthalate.

5 7. The method according to claim 1 wherein said thermal printing means comprises a thermal print head having at least one resistance element between two conductors.

10 8. The method according to claim 7 wherein said latent image pattern is formed by (a) contacting said resistance element to said coating, (b) providing electric current to said resistance element for a time sufficient to heat said resistance element to a temperature that melts
15 said coating at the point of contact, (c) discontinuing the provision of electric current to said resistance element, (d) relocating said resistance element on said coating, and (e) repeating seps (a) through (d) until said latent image pattern is formed.

20 9. The method according to claim 1 wherein said imaging powder comprises a magnetizable powder having a particle size range of about 1 to about 40 microns.

25 10. The method according to claim 9 wherein said imaging powder is insensitive to heat and/or pressure.

30 11. The method according to claim 9 wherein said imaging powder comprises from about 40 to about 45 percent by weight Bisphenol A fumarate, from about 55 to about 60 percent by weight magnetite, and from about 1 to about 2 percent by weight carbon.

35 12. The method according to claim 9 wherein said imaging powder is selected from the group consisting of iron, nickel, cobalt, chromium oxide, magnetite, $\gamma\text{-Fe}_2\text{O}_3$.

13. The method according to claim 9 wherein said imaging powder is selected from the group consisting of alloys of iron, nickel, and cobalt.

5 14. The method according to claim 1 wherein said substrate bears from about 0.5 to about 5 g/m² of said coating.

10 15. The method according to claim 14 wherein said coating is attached to the surface of said substrate.

15 16. The method according to claim 1 wherein said pressure is between about 5 to about 300 grams per square centimeter.

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