United States Patent [19]

Rolker et al.

[11] **3,880,689**

[45] **Apr. 29, 1975**

[54] **MAGNETIC DEVELOPER CONTAINING AN ELECTROLESS PLATING SENSITIZER, AND METHOD OF USING SAME**

[75] Inventors: **John H. Rolker**, Altadena; **Bradley A. Carson**, Monrovia, both of Calif.

[73] Assignee: **Eastman Kodak Company**, Rochester, N.Y.

[22] Filed: **July 19, 1973**

[21] Appl. No.: **380,801**

Related U.S. Application Data

[63] Continuation-in-part of Ser. Nos. 185,109, Sept. 30, 1971, abandoned, and Ser. No. 185,106, Sept. 30, 1971, and Ser. No. 185,104, Sept. 30, 1971, abandoned.

[52] **U.S. Cl.** ..... **156/233;** 427/12; 427/47; 204/15; 346/74 MP; 96/1 E

[51] **Int. Cl.** **G03g 19/00**

[58] **Field of Search** ..... 346/74 MP; 96/1 E; 117/17.5, 212, 235, 239, 130 E, 236, 240, 217, 218, 100 L, 28; 96/1 E; 204/2, 15, 18 PC; 346/74 MP

[56] **References Cited**

UNITED STATES PATENTS

2,884,348	4/1959	Kulesza	134/1
3,120,806	2/1964	Supernowicz	117/212
3,451,128	6/1969	Reed et al.	117/239

OTHER PUBLICATIONS

Craik et al., British Journal of Applied Physics, Vol. 9, pp. 279–282, (1958).

Primary Examiner—Michael Sofocleous
Attorney, Agent, or Firm—D. M. Schmidt

[57] **ABSTRACT**

An improved method of developing magnetic images comprises contacting such an image with a novel developer to develop a visible image. The developer includes a magnetically attractable toner and an electroless plating sensitizer per se or with a binder therefor. The developer image is then electrolessly plated so as to provide it with high density and contrast. Printing off of the developed image can occur before the electroless plating, the copy sheet image being intensified by electroless plating.

14 Claims, No Drawings

MAGNETIC DEVELOPER CONTAINING AN ELECTROLESS PLATING SENSITIZER, AND METHOD OF USING SAME

CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of application Ser. No. 185,109, entitled "Metal Encapsulation," filed Sept. 30, 1971, now abandoned, of application Ser. No. 185,106, entitled "Activation Method for Electroless Plating," filed Sept. 30, 1971 and of application Ser. No. 185,104, entitled "Magnetic Printout Method and Media", filed Sept. 30, 1971 now abandoned.

FIELD OF THE INVENTION

The present invention generally relates to image development and more particularly to the improved development of latent magnetic images to clear, sharp visible images of high contrast and density.

BACKGROUND AND SUMMARY OF THE INVENTION

Magnetic recording or imaging techniques with magnetic printout are well known as may, for instance, be seen from the following U.S. Pat. Nos., which are herewith incorporated by reference herein: 2,793,135, by J. C. Sims et al, issued May 21, 1957, 2,901,309, by R. B. Atkinson et al, issued Aug. 25, 1969, 2,943,908, by J. P. Hanna, issued July 5, 1960, 3,120,806, by E. J. Supernowicz, issued Feb. 11, 1964, 3,161,544, by T. M. Berry, issued Dec. 15, 1964, 3,052,564, by F. W. Kulesza, issued Sept. 4, 1962, 3,250,636, by R. A. Wilferth, issued May 10, 1966, 3,472,695, by H. Kaufer et al, issued Oct. 14, 1969, 3,512,170, by A. M. Nelson, issued May 12, 1970, 3,555,556, by G. R. Nacci, issued Jan. 12, 1971, 3,555,557, by G. R. Nacci, issued Jan. 12, 1971, 3,554,798, by G. R. Nacci, issued Jan. 12, 1971, and 3,582,877, by Luc P. Benoit, issued June 1, 1971. Other prior art includes the following U.S. Pat. Nos., which are herewith incorporated by reference herein: 3,560,257, 3,259,559, 3,231,374, 3,165,420, 2,947,625, 3,218,509, 3,334,000, 3,291,600, 3,329,590, 3,458,310, 3,152,969, 3,268,353, 3,515,649, and 3,524,754.

Visible images produced by magnetic imaging and developing processes often exhibit relatively poor contrast, density and overall resolution due to, for example, poor toner distribution and print-off, weak and/or non-uniform charging of the photoconductive surface, etc. Low image density is particularly a problem with microimages. Accordingly, various procedures, many of which are complicated, expensive and time-consuming, have been developed to improve the quality of the finished visible image. However, there remains a definite need for a simple, rapid and inexpensive procedure which can uniformly provide high quality results. Such procedure should be adaptable to those processes which include the formation of a master developed image from which copies are then made, e.g. microfiche images. The quality of the master determines the upper limit for the quality of the copies. Therefore, the master should be of the highest quality possible.

Another area of interest in photoreproduction is the production of electronic circuitry. Current electrolytic printing resist techniques and the like are complicated and time-consuming and have resolution deficiencies.

It has now been discovered that the quality of visible images obtained in magnetic processes can be greatly enhanced by utilizing in the toner developer a selected sensitizer which permits the visible image to be electrolessly plated. The plating step strengthens the contrast and density of the image while keeping the background density low. The sensitizer is carefully selected so as to provide maximum results with a wide variety of developers.

It has been discovered that most conventional developer for magnetic images can be employed, so long as it includes the sensitizer. The developer can comprise the sensitized toner in dry, particulate form or the sensitized toner may be suspended in a developer liquid as known to the art. The concentration of sensitizer can be kept low, so long as it is sufficient to permit electroless plating of the visible image with copper, nickel, cobalt or other electrolessly plateable metal. The process can be readily applied to microxerographic images to produce high resolution, high contrast masters for use in microfiche and the like. By transferring the toned image to a circuit board, prior to plating, and then plating on the board, one can automatically and readily produce electronic circuits of any configuration and with high resolution. Electroplating the electrolessly plated image can produce any desired thickness of metal for such circuit boards.

The sensitizer is characterized by being one or more compounds of one or more metals of Group IB and VIII of the periodic table and tin, that is, copper, silver, gold, iron, nickel, cobalt, palladium, platinum, iridium, osmium, ruthenium, rhodium and tin. The noble metals are preferred. The selected compounds for the sensitizer are those which are reducible, as in electroless plating solutions, to their active metal constituents so as to form catalytic bonding sites on the visible image for the electroless plating.

The advantages of the present image development method can be incorporated simply and effectively in commercial image developing and copying processes, since the toner can be used in conventional equipment and the plating step is easily carried out. Further features of the present invention are set forth in the following detailed description.

DETAILED DESCRIPTION

In accordance with the present method, a latent magnetic image on a magnetizable surface, e.g. a strip of recorded magnetic tape, is contacted with a novel image developer to develop it to a visible image. The developer comprises a magnetizable toner and the sensitizer previously described. The toner material can be mixed with sensitizer prior to being fully formed or the sensitizer can be applied to fully formed toner by immersion in a solvent-binder solution of the sensitizer. Details respecting the binder, sensitizer, solvents therefor, magnetizable toner, and conditions of preparation are described in our copending applications referred to above, the disclosures of which are incorporated herein by reference.

The unsensitized toner can be any conventional toner or mixture of toners useful for developing a magnetic image and generally comprises a magnetic component and a nonmagnetic component which may be separate, though closely adhered entities or may be part of a single entity. For example, one or two or more magnetic particles can be embodied in a casing of nonmagnetic

material. Suitable materials for the magnetic compound are apparent from the above-mentioned patents and may include particles formed of iron, gamma ferric oxide or magnetite, cobalt, nickel, ferromagnetic chromium dioxide, nickel-zinc ferrite and/or manganese-zinc ferrite. One or more of the particles may be acicular, such as acicular particles which can be formed from gamma ferric oxide, chromium dioxide or other magnetic materials that can be grown or otherwise provided in acicular configuration. Still other suitable materials are those magnetic materials which are formed and/or reactable with nonmagnetic material, such as, for example, obtained by reacting urethane, polybutadiene, or conjugated linseed oil with iron pentacarbonyl, nickel tetracarbonyl or cobalt octacarbonyl, as known to the art, to form metal particles bound to the polymer.

Suitable materials for the nonmagnetic component are disclosed in the above-mentioned Kulesza, Wilferth and Kaufer et al. patents, which disclose thermoplastic or meltable waxes or resins, including paraffins, polyamide resins, polyvinyl resins, and colophony resin. Further suitable resins are disclosed in U.S. Pat. No. 2,891,011, by Insalaco, issued June 16, 1959, or U.S. Reissue Pat. No. 25,136, by Carlson, each of which are herewith incorporated by reference herein. Further suitable materials for the nonmagnetic component 12 include the thermoplastic materials, such as coal pitch, acrylate resins, polystyrene and polyethylene disclosed in U.S. Pat. No. 2,939,804, by Frederick V. Schossberger et al, issued June 7, 1960, and herewith incorporated by reference herein, and cresylic resins, pentaerythritol alkyd resins, and the other resins disclosed in U.S. Pat. No. 3,078,231, by Kenneth A. Metcalfe et al, issued Feb. 19, 1963, and herewith incorporated by reference herein. Still further suitable materials are polyurethanes, polybutadiene and conjugated linseed oil, which, as indicated, can be reacted with iron carbonyl or the like.

The toner particles may be made by dispersing the magnetic particles in the nonmagnetic material. The dispersion may be subjected to ball milling, if necessary with heating and/or a solvent, drying and/or cooling. Roller milling and high speed mixing are alternatives. The resultant particles may be reduced to a desired size by such conventional methods as high-speed air attrition, ball milling with or without a non-solvent, or spray drying by atomizing particles present in an aerosol. Normal toner particles generally have a particle size of 0.05 to 100 microns; those formed from such materials as $Fe(CO)_5$ have a primary (metallic) particle size of about 0.003–0.10 micron.

The toner particles can be sensitized by immersion in a pre-plate solution of the type generally described in our prior copending applications which solutions comprise a binder and a sensitizer compound as more fully described below. The sensitized toner particles can then be separated by filtration, dried and tumbled for separation, or spray-dried. The particles thus formed have a layer of polymer and an electroless plating sensitizer metal in the surface of the polymer layer as catalytic bonding sites for an electroless plating process. The sensitized toner particles can then be used as dry toner or can be suspended in a developer liquid, as known to the art.

In another embodiment, the nonmagnetic component of the toner can serve also as the binder for the above-referred-to pre-plate solution by (1) mixing the sensitizer component with nonmagnetic binder and forming the toner by dispersion therein of magnetic particles as above described; (2) mixing the sensitizer with fully formed magnetic fluid after, there being sufficient binder for both magnetic toner and sensitizer use; and (3) mixing the constituent materials, prior to full formation of the toner particles, with the sensitizer component and solvent of the pre-plate solution. For example, toner particles can be formed by reacting iron pentacarbonyl with polyurethane in a solvent containing the sensitizer, the polyurethane acting both as pre-plate solution binder as well as the nonmagnetic component of the toner. The latter formulations are particularly suitable as liquid toner developers.

When a separate binder is used in the pre-plate solution, one can utilize any of the well known inorganic or organic materials which can be dried and/or cured to form a film. For example, one can utilize such inorganic materials as alkali metal silicates, aluminosilicates, phosphonitriles and polyboranes. As useful organic materials one can utilize condensation-type or addition-type polymer forming materials, including monomers which form such polymers. Examples include: cellulose derivatives, such as cellulose nitrate, cellulose acetate and ethyl cellulose; phenolformaldehyde resin; polyamide resins, such as nylon and polymers obtained from dimerized fatty acids; polyester resins, such as alkyds, unsaturated polyesters, polyethylene terephthalate, aromatic polycarbonates and polydiallyl esters; polyether resins, such as epoxy resins, polyethylene oxide, polypropylene oxide, phenoxy resins, polyphenylene oxide resins, polyoxymethylene and chlorinated polyethers; polysulfide resins; polysulfone resins; polyurethane resins; silicone resins, such as polydimethylsiloxane; amino resins, such as urea-formaldehyde resin, melamine-formaldehyde resin; heterocyclic polymers, such as polyvinylcarbazole; polybenzimidazoles and polybenzothiazoles; polyacrylate resins, such as polymethyl methacrylate, polyethyl acrylate, methyl chloroacrylate, cyclohexyl methacrylate and polymethyl-2-cyanoacrylate; polyacrylonitrile resins; acrylonitrilebutadiene resins; polyfluoroolefin resins such as polytetrafluoroethylene, polymonochlorotrifluoroethylene, polyvinylidene fluoride and fluorinated elastomers; polyolefin resins such as polyethylene, polypropylene, polyisobutylene; polypentene-1, poly-4-methylpentene-1, polybutadiene, poly-3-methylbutene-1, polyisoprene and poly-2-chlorobutadiene; polystyrene resins; polyvinyl resins, such as polyvinyl chloride, polyvinyl acetate, polyvinylidenechloride, polyvinyl alcohol, polyvinyl acetals, polyvinyl ethers, polyvinyl fluoride, polyvinyl pyrrolidone, polyvinyl carbazole and polyvinyl cinamate; and naturally formed hydrophilic materials, such as starch and starch derivatives, proteins (i.e., casein, zein, gelatin, thiolated gelatin, and the like), alginates, gums and the like.

Fusible polymeric binders such as polyethylene, polyvinyl chloride, polystyrene, acrylic polymers and the like can be used in a dry developer without a solvent system, if desired.

Generally, the polymer former is used in its liquid state, when it is somewhat polymerized but not fully cross-linked, but if soluble may be used in its fully reacted state, or the material may be used in its monomeric state. Mixtures of polymers and/or monomers, as

well as copolymers, can be utilized. Examples of heat decomposable polymers include polymethyl methacrylate, urethanes, especially those prepared from polyhydroxy aromatics, polyvinyl cinnamate, diazo polymers, urea-formaldehyde resins, polyvinyl alcohols, shellac, and the like. Other polymers can be chosen by actual experimentation or by reference to "Stabilization of Synthetic High Polymers" (1964) by G. Y. Gordon (translated from the Russian by A. Mercado), published by Daniel Davey & Co., Inc., New York, N.Y., incorporated herein by reference.

The sensitizer is, as previously described, one or more compounds of one or more noble metals of Groups IB and VIII of the periodic table and tin, namely copper, silver, gold, iron, nickel, cobalt, palladium, osmium, iridium, ruthenium, platinum, rhodium and tin. Palladium, platinum, gold and silver are preferred, with palladium most preferred. The compounds referred to are those which are reducible to yield the noble metal thereof, thus forming catalytic bonding sites on the visible developed image. Examples of such compounds are palladium chloride, palladium acetate, palladium allyl chloride, palladium nitrate, palladium trimethylbenzyl ammonium nitrate, palladium hydroxide, platinum dicarbonyl chloride, platinum tetrachloride, silver nitrate, platinum acelytacelonate, trimethyl platinum bromide, silver citrate, silver cyanide, auric chloride, and auric cyanide. Generally, about 0.0001 to about 1 percent by weight of the metal component of the catalytic compound is present in the pre-plate solution and the weight ratio of sensitizer to binder is from about 1:0.3 to about 1:15.

A single solvent may be used to dissolve both the metal compound and binder material. For example, acetone can be used to dissolve both palladium chloride and polyvinyl chloride. On the other hand, particular metal compounds may be insufficiently soluble in a solvent which is most suitable for a particular polymer former. In such case, one can simply choose a solvent for the metal compound which is soluble in the binder-dissolving solvent. For example, palladium acetate as the metal compound may be dissolved in benzene and then added to a cyclohexanone solution of a polyester bis (phenylisocyanate) methane and polyurethane. Other particular solvents can be chosen in accordance with the solubilities of the materials desired to be combined, which solubilities can be readily determined. Any of the common vaporizable solvents can be utilized, including alcohols such as methanol, ethanol, and the like, acetones and other ketones such as methyl ethyl ketone, methyl isobutyl ketone and cyclohexanone, halogenated hydrocarbons such as chloroform and carbon tetrachloride, diethyl ether, xylene, toluene, benzene, dimethyl formamide, dimethyl sulfoxide, cellosolve acetate, methyl cellosolve acetate, hexane, ethyl acetate, isophorone, mesityl oxide, tetrahydrofuran, cumene, and the like, and combinations thereof.

Methods of printing out a magnetic record with developers are well known. For example, a magnetic information record can be provided in any conventional manner on a magnetic recording medium, such as ferromagnetic chromium dioxide, supported on a suitable substrate. Examples of conventional recording techniques and recording media are given in the abovementioned Atkinson et al, Hanna, Supernowicz and Berry patents. Examples of thermomagnetic recording techniques and media are given in the abovementioned Sims et al, Wilferth, Nelson, Nocci and Benoit patents.

Magnetic information records thus obtained are sometimes referred to as "latent", since the magnetic record as such is, of course, not visible. To develop the latent record, the surface of the magnetic recording medium bearing the latent record is contacted with a developer composition of the present invention by spraying or dusting the developer onto the recording medium surface, immersing the latter in liquid developer or by an equivalent procedure. Contacting is carried out for a time sufficient to assure proper development of the image to a visible state, after which the excess developer is removed, as by rinsing, vibration, or the like, followed by air drying to remove excess solvent. Toner is attracted to the record surface by magnetic moments of the record and, accordingly, form a toner image corresponding to the magnetic record. The toner image can be fixed on the surface of the record by continuing the air drying to remove all solvent, or, in the case of dry developer, by heating the record surface sufficiently to fuse the fusible binder. Alternatively, fixing can occur after the toner image is transferred or printed off to one of a plurality of receiving sheets. For example, the image can be transferred to a triacetate film previously coated (subbed) with acrylic polymer or the like adhesive dissolved in a solvent such as toluene. The transfer can occur, for example, by pressing the receiving sheet's adhesive coating against the toner image on the record surface while both are passed through the pressure gap in a pair of steel rollers. Control of proper pressure is necessary in order to assure complete image transfer without distorting or blurring the transferred image. As above indicated, the image can be printed off onto a circuit board or the like. Reference may be made to the above-mentioned Hanna, Berry, Wilferth and Benoit patents for examples of specific procedures.

In accordance with the present method, the toner image on the original photoconductive surface or receiving sheet surface is then electrolessly plated to increase its density and contrast. Conventional and other suitable electroless plating solutions can be used which reduce the sensitizer to the catalytic metal contained in the sensitizer compound to provide the desired bonding sites on the visible image. Usually a copper, nickel or cobalt electroless plating solution or one which contains a combination of two or more of these metals will be used, as by contacting it with the visible image and then removing it after the desired plating is accomplished, usually in 4 minutes or less at ambient temperature. Alloys of nickel-iron, nickel-cobalt and nickel-tungsten-phosphorous have been successfully plated on the visible image, either in single or in multiple layers. If a magnetic image is desired, a magnetic metal such as cobalt or iron suitable alloys can be electrolessly plated. Upon removal from the electroless plating solution and drying, the plated image is ready for use as a finished image rendition or as a master from which copies can be made.

Certain further features of the invention are illustrated in the following specific Examples:

EXAMPLE 1

One hundred ml. of a liquid magnetic toner developer is mixed with 15 ml. of a 1 percent by weight solution of palladium chloride in acetone. The developer comprises about 5 percent by weight of polyurethane

reacted with iron pentacarbonyl, $Fe(CO)_5$ to form a magnetic homogeneous fluid comprised of small (e.g. less than 100 A) iron particles bound to the urethane polymer. Some such urethane polymers are commercially available from B.F. Goodrich under the trademark "Estane."

Latent electrostatic images previously formed on high resistivity anhysteretically demagnetized chromium dioxide tape (by exposure to 100V/mil electric image field) are developed by passing the exposed tape into the liquid developer, holding the tape therein for a short period, e.g., less than 2 seconds, then removing the tape, rinsing it with toluene and air drying it. The now visible image is transferred to a film base coated with an acrylic polymer adhesive by passing the tape and film base, face to face (coating-to-image), through a pair of steel pressure rollers. The transferred image is then copper plated on the film base in a commercial electroless plating bath available from the Shipley Co. under the trademark "Cuposit 328 (AB&C)." The electroless plating is carried out in about 1.5 minutes at about 77°F. The copper plated image is found to be dense, sharp, of high contrast with the film background and of overall much higher quality than comparable images not electrolessly plated.

EXAMPLES 2–11

The procedure of Example 1 can be repeated, but substituting another sensitizer for the palladium chloride and using suitable solvents for the sensitizer as listed below:

Example	Sensitizer	Concentration of Sensitizer (Wt.%)
2	Palladium acetate	0.8 in Dimethylformamide
3	Palladium allyl chloride dimer	0.8 in Benzene
4	Platinum acetyl acetonate	1.6 in Acetone
5	Platinum tetrachloride	1.6 in Methyl alcohol
6	Tin dibromide	1.6 in Acetone
7	Cuprous chloride	1.6 in Cyclohexanone
8	Silver perchlorate	1.6 in Ethyl alcohol
9	Silver nitrate	1.6 in Ethyl ether
10	Auric bromide	1.6 in Ethyl ether
11	Cuprous nitrate	1.6 in Ethyl alcohol

Comparable results to those described above are obtainable.

EXAMPLE 12

The procedure of Example 1 is carried out except that the urethane solution contains 10 ml. of 1 percent palladium chloride in acetone and 3 ml. of 1 percent palladium acetate in dimethyl formamide. The magnetically recorded chromium dioxide tape is merely dipped into the developer, then rinsed with toluene, air dried and the visible image thereon is transferred to 5 mil. thick acetate film coated with acrylic resin (5% in toluene). The transferred image is then electrolessly plated with copper, as in Example 1, to provide a high contrast image. Exposure of the copper layer to ammonium sulfide blackens the copper, and further enhances the image contrast with the film background.

EXAMPLE 13

The procedure of Example 1 is carried out, except that electroless plating is carried out for 3 minutes at room temperature in a bath containing 3.5% $CoSO_4$, 7.0% $Al_2(SO_4)_3$, 2.0% NaH_2PO_2 and 15.0% NaK tartrate. A high contrast image is obtained.

EXAMPLE 14

The procedure of Example 1 is carried out, except that a nickel electroless plating bath is used at 120°F. for 1 minute, the bath having the following composition: 2.5 weight percent $NiSO_4.6H_2O$, 5.0 weight percent $Na_4P_2O_7$, 2.5 weight percent NaH_2PO_2 and NaOH to pH 10. Results comparable to those of the previous Examples are obtainable.

EXAMPLE 15

A dispersion of magnetite particles in polystyrene of the type sold by the Pennsylvania Industrial Co. under the designation Picco D–100 is made by high-shear agitation of the molten polystyrene at 150°C with the magnetite particles. This dispersion is cooled with agitation until the magnetite particles are well dispersed and firmly held by viscous forces. The resulting pigmented mass is crudely broken up with a grinder when at 100°C, and then attrited to 5 to 10 micron size with a high-speed air attritor. In this manner, toner particles are produced in which the magnetic component is provided by magnetite particles and in which the toner component is provided by the polystyrene as a fusing agent (and also, visibility is provided by the magnetite particles as a pigmenting agent).

A pre-plate solution is prepared by dissolving 0.1 parts of palladium acetate and 0.5 parts of polyvinyl alcohol in 200 parts of dimethylformamide. The above prepared toner particles are placed into this pre-plate solution, which is stirred until the core particles are wetted and a suspension of the particles is formed. The suspension is then filtered under vacuum and the core particles are placed in a forced air oven at about 40°C until dry. Small conglomerated chunks are broken up and the core particles are then dusted onto a record as referred to in Example 1. The now visible image is transferred to a film base and electrolessly plated with copper as described in Example 1.

EXAMPLE 16

The procedure of Example 15 is followed except that the toner particles are prepared by stirring together equal parts of white beeswax and iron oxide particles with heating to about 80°C. The mixture is solidified by being poured, while being stirred, into liquid nitrogen. The solidified mixture is ground into small particles in a Waring blender while liquid nitrogen is added. The resulting particles are then sensitized and utilized as set forth in Example 15.

Since the electroless plating step is rapid and simple and since the use of the sensitizer-containing developer in place of conventional developer does not entail any additional time or equipment, the improved results in image clarity and contrast as obtained with the present method demonstrates a simple, inexpensive, direct method suited to commercial use.

In each of the foregoing Examples, the electrolessly plated images can be further plated by electrolytic

means, as well known to the art, to provide any desired thickness of plated image.

What is claimed is:

1. An improved method of developing magnetic images, said method comprising:

contacting a latent magnetic image on a magnetic record surface with an image developer comprising a magnetically attractable toner having a magnetic component and a nonmagnetic component, said toner being sensitized with a metallic electroless plating sensitizer comprising a compound of a metal selected from tin and metals of Group IB and VIII of the periodic table and mixtures thereof, capable of being reduced to an active metal constituent which is a catalyst for electroless plating, said contacting being effected for a time sufficient to develop said image; and

electrolessly plating said developed image to provide it with density and contrast.

2. The improved method of claim 1 wherein said metal is selected from the group consisting of tin, copper, silver, gold, iron, nickel, cobalt, ruthenium, rhodium, palladium, osmium, iridium, platinum and mixtures thereof.

3. The improved method of claim 2 wherein said metal is palladium.

4. The improved method of claim 3 wherein said sensitizer comprises palladium chloride.

5. The improved method of claim 3 wherein said sensitizer comprises palladium acetate.

6. The improved method of claim 1 including the steps of preparing said sensitized toner, said steps comprising:

applying to unsensitized particles of said toner a combination comprising a metal compound capable of being reduced to its active metal constituent so as to form catalytic bonding sites for an electroless metal plating process, binder material comprising one or more polymers and/or polymer formers and a solvent for said binder material and metal compound, to coat said particle therewith; and

separating said coated toner particles from said solvent.

7. The improved method of claim 6 wherein said metal is selected from the group consisting of tin, copper, silver, gold, iron, nickel, cobalt, ruthenium, rhodium, palladium, osmium, iridium, platinum, and mixtures thereof.

8. The improved method of claim 7 wherein said metal is palladium.

9. The improved method of claim 1 including the step of preparing said sensitized toner, said step comprising combining a metal compound capable of being reduced to its active metal constituent so as to form catalytic bonding sites for an electroless metal plating process, binder material comprising one or more polymers containing a magnetically attractable material and a solvent for said binder material and reducible metal compound.

10. The improved method of claim 9 including the step of preparing said binder material containing a magnetically attractable material, said step comprising reacting a precursor compound of said magnetically attractable metal with said one or more polymers.

11. The improved method of claim 9 including the steps of drying said binder material-reducible metal compound and forming toner sized particles therefrom.

12. The improved method of claim 9 wherein said metal is selected from the group consisting of tin, copper, silver, gold, iron, nickel, cobalt, ruthenium, rhodium, palladium, osmium, iridium, platinum, and mixtures thereof.

13. The improved method of claim 12 wherein said metal is palladium.

14. A method of producing a fixed magnetic image, comprising the steps of:

contacting a latent magnetic image on a magnetic record surface with an image developer comprising a magnetically attractable toner having a magnetic component and a nonmagnetic component, said toner being sensitized with a metallic electroless plating sensitizer comprising a compound of a metal selected from tin and metals of Group IB and VIII of the periodic table and mixtures thereof, capable of being reduced to an active metal constituent which is a catalyst for electroless plating, said contacting being effected for a time sufficient to develop said image,

electrolessly plating said developed image to provide it with density and contrast, and

printing off the developed image from the record surface onto a receiving surface prior to said step of electrolessly plating.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,880,689

DATED : April 29, 1975

INVENTOR(S) : John H. Rolker and Bradley A. Carson

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 10, insert after "most", ---any---.

Column 5, line 44, "and" should read ---based---.

Signed and Sealed this

twenty-sixth Day of *August 1975*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks