July 2, 1974 MASAYOSHI TSUBOI ET AL 3,822,127
PROCESS OF PRODUCING METAL IMAGES BY AMPLIFICATION OF DIFFUSION TRANSFER IMAGES
Filed Dec. 29, 1971

FIG. 1

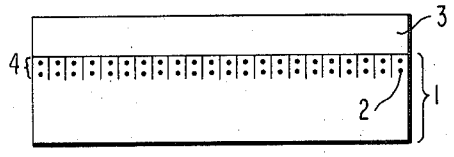


FIG. 2

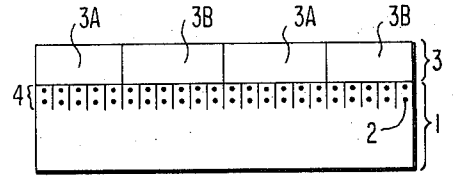


FIG. 3

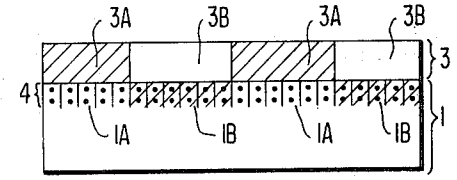
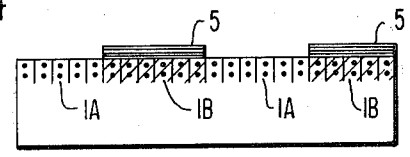


FIG. 4



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PROCESS OF PRODUCING METAL IMAGES BY AMPLIFICATION OF DIFFUSION TRANSFER IMAGES

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Int. Cl. G03c 5/54
U.S. Cl. 96—29 R 13 Claims

ABSTRACT OF THE DISCLOSURE

A process for producing metal images comprising image-exposing, through an original image, a photosensitive element which comprises a photosensitive silver halide photographic emulsion laid on a hydrophilic surface of a plastic which has a surface containing a diffusion transfer nucleus material forming reversal silver images of the original on the surface by a diffusion transfer developing process and intensifying said silver images by electrolessly plating a metal thereon.

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a process for producing a photographic image forming base plate and, in more detail, to a process for producing metal images which comprises carrying out electroless plating corresponding to silver images formed on a plastic surface.

Description of the Prior Art

In U.S. Pat. 3,033,765, Japanese Pat. Pub. No. Sho 45–25234 and British Pat. 1,183,907, processes for producing electrically conductive silver images on a surface of a silver halide photographic emulsion are described. However, in these processes, specific chemicals are required, e.g., a hydrophilic organic colloid layer which easily absorbs moisture from the air, is exposed to the air by which it becomes soft and sticky. The electrically conductive silver images are produced on the hydrophilic organic colloid layer, which is a material such as gelatin or polyvinyl alcohol, and consequently the images are difficult to handle, and are easily injured. Furthermore, the electrical resistivity of such electrically conductive surface images is higher than that of conventional printed circuits and printing base plates.

SUMMARY OF THE INVENTION

According to the process of producing metal images of the present invention, the faults shown in the prior art can be removed so that it becomes possible to produce electrically conductive metal images having a lower electric resistivity and thermally conductive images having a good thermal conductivity.

Such metal images can be produced by a process which comprises exposing a photographic image-forming base plate prepared by applying a photosensitive silver halide photographic emulsion onto a hydrophilic surface of a plastic film which contains a nucleus substance for a diffusion transfer process, producing reversal silver images of the original on said hydrophilic surface part by the diffusion transfer process, removing the silver halide photographic emulsion layer, and "intensifying" the reversal silver images by electroless plating.

The present inventors have thus found that the electroless plating can be carried out on silver images photographically produced on a hydrophilic part of a plastic having a hydrophilic surface part. Furthermore, they have found that such silver images can be produced on plastics having an oleophilic surface whereafter electroless plating can be practiced on said silver images.

One object of the present invention is to provide a process producing metal images by producing silver images photographically on a surface of a plastic, and thereafter practicing the electroless plating on said silver images (hereinafter, to plate the silver images with metal by electroless plating is called "intensification").

Another object of the present invention is to produce electrically conductive surface images by "intensifying" the silver images produced on the surface of a plastic.

A further object of the present invention is to produce metal images having a good thermal conductivity by "intensifying" the silver images produced on the surface of a plastic.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a sectional view of a photographic image-forming base plate used in the present invention;

FIG. 2 shows a state of exposing this base plate;

FIG. 3 shows a photographic image forming base plate after treating with a diffusion transfer developer; and

FIG. 4 shows a photographic image forming base plate after electroless plating treatment.

DETAILED DESCRIPTION OF THE INVENTION

Regarding the degree of the hydrophilicity, any plastic is applicable provided that a diffusion transfer developing solution is permeable to silver halide photographic emulsion and that alkali solution is chemically permeable.

The degree of the hydrophilicity at the hydrophilic surface of the plastic film or the plastic laminating layer can be indicated by, for example, a static contact angle toward the distilled water.

The following data is obtained by determining the static contact angle of the liquid drop of the distilled water fallen on a film at 25° C. in one minute using a microscope.

TABLE

	Film surface	Static contact angle, degrees
1	Cellulose triacetate (TAC) film (125μ)	55
2	TAC film, the surface of which was processed with 10% sodium hydroxide solution at 70° C. for one minute, washed with water and dried.	22
3	Cellulose diacetate (DAC) film	59
4	DAC film, the surface of which was processed with 5% sodium hydroxide (water/methanol=1:1) solution at 25° C. for one minute, washed with water and dried.	35
5	DAC film, the surface of which was treated in the same manner as in 4 but for two minutes.	22
6	Polyethylene terephthalate (PET) film (100μ)	70
7	PET film passed through a propane gas-oxygen flame at a rate of 100 m./min.	48
8	Polyethylene (PE) film	93
9	PE film treated with corona discharge at 70 W. using an electrode having 30 cm. in width at a distance of 1 mm.	55
10	TAC film processed with coating and hardening	27
11	Polystyrene (PS) film	82
12	PS film treated with corona discharge at a rate of 200 W./2 m.	15

Besides polyvinyl alcohol, the hydrophilic film includes partially saponified polyvinyl alcohol film, partially saponified hydroxyethyl polyvinyl alcohol film, cellophane, polyethylene laminated cellophane, anti-humidity cellophane, polyethylene oxide films, methyl cellulose films and gelatin film.

If the entire film is not hydrophilic such as TAC, the hydrophilic portion must be thick more than 0.05μ, preferably more than 0.1μ, which was confirmed by an electron microscope.

In the present specification, the term "hydrophilic surface part" includes the following three cases.

(1) Plastic films wherein only the surface is treated to render the same hydrophilic, e.g., with a chemical agent, by corona discharge processing or by flame treatment.

Example (1–a)

A cellulose organic acid ester sheet which is originally oleophilic (cellulose acetate, cellulose propionate, cellulose butyrate, cellulose acetate propionate and cellulose acetate butyrate) is contacted with an aqueous solution of an alkali, a mixture of alkali containing water or a solvent or an alkali containing solvent. There will result a cellulose organic acid ester sheet only the surface of which becomes hydrophilic. In this case, the degree of hydrophilic property in the thickness direction of the sheet is not uniform, but lowers continuously from the surface to the interior of the sheet.

Example (1–b)

Polyethylene terephthalate film is treated by flame treatment to give the same decreasing hydrophilic property.

Example (1–c)

A polyethylene film is treated by corona discharging to give the same decreasing hydrophilic property.

(2) Oleophilic plastic films to a surface of which a hydrophilic binder is applied.

Example (2–a)

A cellulose triacetate film to which gelatin or polyvinyl alcohol is applied.

Example (2–b)

A polyester film to which a vinyl chloride-vinyl acetate copolymer is initially applied and casein thereafter applied.

(3) Hydrophilic plastic films. For example, a polyvinyl alcohol film.

These hydrophilic surface parts are made to contain diffusion transfer nuclei. Examples of diffusion transfer nuclei are, for example, colloidal heavy metals such as colloidal silver, sulfur compounds such as silver sulfide, nickel sulfide, cadmium sulfide and zinc sulfide and selenium compounds such as silver selenide and nickel selenide, which are known substances commonly used in diffusion transfer processes. The diffusion transfer nuclei may be introduced after production of the hydrophilic surface or may be added at the film forming process before carrying out the hydrophilic treatment. Further, the diffusion transfer nuclei may be introduced into the hydrophilic surface part after application of a hydrophilic binder such as gelatin, gelatin derivatives, polyvinyl alcohol, casein, carboxymethyl cellulose and alginic acid, or the above-mentioned hydrophilic binder to which the diffusion transfer nuclei are added may be applied onto a surface of the oleophilic plastic films. The minimum thickness of the hydrophilic layer containing diffusion transfer nucleus material is equal to the thickness of the hydrophilic layer or less than the thickness of the hydrophilic layer. The thickness of the hydrophilic layer is more than 0.25μ, preferably more than 0.4μ, it is confirmed by an electron microscope.

One embodiment of the present invention will now be explained referring to the drawings.

FIG. 1 shows a sectional view of a photographic image forming base plate used in the present invention, in which an oleophilic plastic sheet (for example, a cellulose organic acid ester sheet) **1** has a hydrophilic surface part **4** containing diffusion transfer nuclei **2** and a photosensitive silver halide photographic emulsion layer **3** applied thereto.

FIG. 2 shows the exposed state of the photographic image forming base plate of FIG. 1 which has been exposed to light through an original. In the emulsion layer **3**, **3A** represents an exposed part, that is a part corresponding to a non-image part of the original, and **3B** represents a non-exposed part, that is, a part corresponding to an image part of the original. As the original, line drawings or half-tone images may be used. Exposure may be carried out directly from a continuous gradation original using a screen. Exposure may be practiced by contact printing or enlarging.

The exposed photographic image forming base plate is then treated by a diffusion transfer development. The developer which is used in the common diffusion transfer process contains a silver halide solvent together with a developing agent. Representative silver halide solvents are, for example, thiosulfate compounds, thiocyanate compounds, and sodium sulfite.

FIG. 3 shows the photographic image forming base plate after treating with the diffusion transfer developer, in which silver images are formed on exposed parts **3A** of the emulsion layer. These images are negative to the original. On the other hand, silver images **1B** are formed on the hydrophilic surface part **4** underneath unexposed parts **3B** of the emulsion layer. These images are positive to the original, and are produced by diffusion of the complex salt of silver halide from the non-exposed parts **3B** to the hydrophilic surface part **4** containing the diffusion transfer nuclei material **2** by silver halide solvent included in the developer, by which the complex salt is reduced at the site of the nuclei material **2** by the developing agent to produce metallic silver **1B**. The developed photographic image base plate is treated with warm water to remove the emulsion layer **3**. "Complex salt of silver halide" means "silver complex compound," that is, soluble silver complex salt, for example, $Ag(S_2O_3)^-$, $Ag(S_2O_3)_2^{3-}$, $Ag(S_2O_3)_3^{5-}$, $Ag(SCN)_2^-$, etc.

FIG. 4 shows the state of the photographic image forming base plate after plating following removal of the emulsion layer **3**. By the electroless plating, metal silver images **1B** formed in the hydrophilic surface **4** are intensified by metal images **5**.

As the organic colloid for the silver halide emulsion layer used in the present invention, gelatin or other natural or synthetic colloidal binders may be used. The binder having a generic criteria is alkali permeable binder, hydrophilic binder or gelatin compatible binder. Such binders include water-permeable or water-soluble polyvinyl alcohol and derivatives thereof, for example, partially saponified polyvinyl acetate [the one part of polyvinyl alcohol is saponified, and the other parts of polyvinyl alcohol are formed hydroxyl group. See the following.

Polyvinyl ether and acetals which contain many grafted groups —CH_2CHOH— [graft-copolyymerized to many functional groups in polymer chain] and interpolymers of vinyl acetate and an addition-polymerizable unsaturated compounds such as maleic anhydride, ethyl acrylate, ethyl methacrylate and styrene. The colloids lastly described type are disclosed in U.S. Pats. 2,276,322, 2,276,323 and 2,347,811. Preferred polyvinyl acetals include polyvinyl acetaldehyde acetal, polyvinyl butyraldehyde acetal and polyvinyl sodium o-sulfobenzaldehyde acetal. Other useful colloidal binders include poly-n-vinyl lactams as described in U.S. Pat. 2,495,918, copolymers of N-acrylamide alkylbetaine as described in U.S. Pat. 2,833,050, cellulose ethers and esters, colloidal albumin, zein and polyacrylamide.

Similarly, the silver halide emulsions can contain silver chloride, silver bromide, silver iodide or mixtures thereof, and can be selected from the known emulsions containing optical sensitizers, chemical sensitizers, antifogging compounds, emulsion hardening agents, plasticizing compounds, wetting agents, toning agents and frosting agents.

In order to enhance resolving power and prevent halation, an antihalation layer can be applied to the back of the support.

The metal images produced as above may be electrically conductive surface images and thermally conductive surface images. The conductivity of the metal images is less than 6 Ω/square, preferably less than 2 Ω/square. The difference is preferably 100 times between the conductivity of the metal images and that of the backgrounds (non-image parts).

The silver images formed as shown in FIG. 3 are sometimes electrically conductive, but the electrical conductivity thereof is inferior to that of metal images produced by intensification, and the surface of the silver is easily injured. On the contrary, the conductivity of the metal images produced by intensification can be controlled by conditions of the electroless plating treatment and the metal images are difficult to injure. The plating thickness is important criterion, and is controlled by composition of the electroless plating bath, pH and temperature of bath. That composition contains an amount of the metal salt, a kind of the reducing agent and an amount of the reducing agent, pH control-agent, complexing agent, reaction accelerator, etc.

The term electroless plating is also called chemical plating, and any metal such as nickel, copper, chromium, cobalt and tin may be used for intensifying the silver images of the invention. Silver images produced by the prior art as described in U.S. Pat. 3,033,765, Jap. Pat. Pub. No. Sho 45–25234 and British Pat. 1,183,907, or silver images formed on a multi-layer film as described in Jap. Pat. Pub. No. Sho 45–29876 have the faults that it is difficult to intensify with metal images by electroless plating, that the background is soiled at intensification and intensification is weak.

As electroless plating procedures, common methods are described in "Boshyokumekki to Kagakumekki" written by Boshin Ro, published by Daily Industry Newspaper Office (1961) and "Electroless Copper Plating, American Electroplaters' Society," Vol. 46, pages 264–276 (1959) written by E. B. Saubestre can be used. A common process of electroless plating will now be described. After a sheet having metal silver images as shown in FIG. 3 is activated by dipping in an aqueous formalin solution and then in an aqueous solution of a noble metal compound (e.g., 2% palladium chloride; pH 2.0), the sheet is dipped in a copper electroless plating solution, by which the silver images are plated with metal copper. In this process, though the treatment of dipping in the aqueous formalin solution is not always required, it is possible to make rather sharp metal images by this treatment. In the case where the metal silver images formed in FIG. 3 are connected continuously, it is possible to carry out electrolytic plating instead of electroless plating.

The following process may be employed when the silver metal image is electroless plated.

(1) sensitizing by solution of Sn^{2+} or Ti^{3+};
(2) activating by solution of metal salt, said metal salt is palladium (II) chloride [$PdCl_2$], hydrogen gold (IV) chloride [$HAuCl_4$], diaminesilver nitrate [$Ag(NH_3)_2NO_3$], etc.;
(3) plating bath by copper electroplating, nickel electroplating, silver electroplating, gold electroplating, etc.

The present invention may not require sensitizing and hardly requires activating. The activating will result in easy plating on the silver metal.

In the present invention, plating bath includes electroless plating bath of plastics, preferably electroless plating bath of low temperature type, and said temperature is less than the softening point of plastics.

Examples of the said electroless plating bath are as follows.

A. NICKEL PLATING BATH

I. Nickel electroless plating bath

(1) A. Brenner's bath:

Nickel sulfate	g./l.	40
Sodium citrate	g./l.	24
Sodium acetate	g./l.	14
Sodium hypophosphite	g./l.	20
Ammonium chloride	g./l.	5
pH		5.5
Temperature	° C.	40 to 60

(2) H. Narcus's bath:

Nickel sulfate	g./l.	35
Sodium citrate	g./l.	10
Sodium acetate	g./l.	10
Sodium hypophosphite	g./l.	15
Magnesium sulfate	g./l.	20
Duponol C 1% solution	ml.	10

(3) L. Dominikov's bath:

Nickel sulfate	g./l.	20
Sodium citrate	g./l.	45
Sodium hypophosphite	g./l.	20
Ammonium chloride	g./l.	30
Ammonia water	ml.	50 to 55

(4) K. Lang's bath:

Nickel sulfate	g./l.	30
Sodium citrate	g./l.	10
Sodium succinate	g./l.	20
Sodium acetate	g./l.	20
Diethylaminoborazane	ml.	3
Methanol	ml.	50
Stabilizer	g./l.	0.01

II. Nickel electroless plating bath containing boron hydroxide compound

(1) USP 2,942,990:

Nickel sulfate	g./l.	20
Potassium sodium tartrate	g./l.	40
Sodium boron hydroxide	g./l.	2.3
pH (by NaOH)		12.5
Temperature	° C.	40 to 50

(2) USP 2,999,296:

Nickel sulfate	g./l.	50
Lactic acid	g./l.	25
Sodium citrate	g./l.	25
N-dimethylborazane	g./l.	2.5
Wetting agent (bubble-less)	g./l.	0.1
Thioglycol acid	g./l.	1.5
pH (by NH_4OH)		7.0

(3) K. Lang's bath:

Nickel sulfate	g./l.	30
Ethylenediamine	g./l.	60
Sodium hydroxide	g./l.	40
Sodium boron hydroxide	g./l.	0.6
Stabilizer		(1)
pH		--
Temperature	° C.	90 to 95

[1] A small amount.

(4) Lang's bath:

Nickel sulfate (or nickel chloride)	g./l.	30
Sodium citrate	g./l.	10
Sodium succinate	g./l.	20
Sodium acetate	g./l.	20
Diethylborazane	ml.	3
Methanol	ml.	50
Stabilizer	g./l.	0.01
pH		6 to 7
Temperature	° C.	65

III. Nickel electroless plating bath containing hydrazine

(1) USP 2,430,581:

	Parts
Nickel formate (1% solution)	10
Hydrazine hydrate (85% solution)	1
Sodium hypophosphite (saturated solution)	1
Benzyltrimethyl ammonium hydroxide (42% solution)	1

(2) D. J. Levy's bath:

Nickel chloride mol./l.	0.02
Sodium tartrate mol./l.	0.02
Hydrazine mol./l.	1
pH	10
Temperature ° C.	95
Plating rate μ/hr.	3.6

(3) J. W. Diminir's bath:

Nickel acetate g./l.	60
Glycol acid g./l.	60
EDTA (ethylenediaminetetraacetic acid) g./l.	25
Hydrazine ml./l.	100
pH	11
Temperature ° C.	90
Plating rate mill/hr.	0.5

IV. Low temperature nickel electroless plating bath (hypophosphite type)

(1) USP 2,940,018:

Nickel hypophosphite g./l.	26.7
Boric acid g./l.	12
Ammonium sulfate g./l.	2.6
Sodium acetate g./l.	4.9
pH	5.5 to 6.0
Temperature ° C.	21
Plating rate mill/hr.	0.04

(2) M. Schwartz's bath:

Nickel sulfate g./l.	25
Sodium pyrophosphate g./l.	50
Sodium hypophosphite g./l.	25
Ammonia water	
pH	10 to 11
Temperature ° C.	65 to 75
Plating rate mill/hr.	0.6

(3) E. B. Sanbestre's bath:

Nickel sulfate mol./l.	0.005 to 0.2
Sodium hypophosphite mol./l.	0.01 to 0.4
Fluoride mol./l.	0.2 to 1.0
Alkylamine or alkanolamine	(1)
Carboxylic acid salt	(2)
pH	7 to 11

[1] One to 10 times of nickel.
[2] One to 10 times of hypophosphite.

(4) Aoki's bath:

Nickel sulfate mol./l.	0.1
Ethylene diamine mol./l.	1.0
Sodium hypophosphite mol./l.	0.1
pH	6 to 7

V. Alkali nickel electroless plating bath

	Ammoniacal-alkali plating bath			Caustic-alkali plating bath	
	(1) (g./l.)	(2) (g./l.)	(3) (g./l.)	(4) (mol./l.)	(5) (mol./l.)
Composition:					
Nickel chloride	30	45	30	0.1	0.1
Sodium hypophosphite	10	11	10	0.2	0.2
Sodium citrate		100	[1] 65	0.2	0.2
Ammonium chloride	50	50	50		
Boric acid or borax				[2] 0.1	[3] 0.5
pH	8–10	8.5–9.5	8–9	8–9	8–9
Temperature (° C.)	90	90–100	90	90	90
Plating rate (mill/hr.)	0.3	0.6	0.2	0.4–0.5	

[1] Ammonium salt.
[2] Borax.
[3] Boric acid.

B. COPPER PLATING BATH: COPPER ELECTROLESS PLATING BATH

(1)

A solution:	G./l.
Copper sulfate	35
Caustic soda	49
Potassium sodium tartrate	170

B solution—formalin 37% solution.

Dipping at 3 to 15 min. at normal temperature in mixture of the solution of A and B solution, said mixture ratio of A/B is 5/1.

(2)

A solution:

Copper sulfate g./l.	14
Nickel chloride g./l.	4
Formalin 37% solution ml./l.	53

B solution:

Potassium sodium tartrate g./l.	45.5
Caustic soda g./l.	9.0
Sodium carbonate g./l.	4.2

Dipping at normal temperature in mixture of A and B solution, said mixture ratio of the solution A/B is 1/3.

(3)

Copper sulfate g./l.	29
Sodium carbonate g./l.	25
Potassium sodium tartrate g./l.	140
Mixture of EDTA and triethanolamine g./l.	17
Caustic soda g./l.	40
Formalin 37% solution g./l.	166

(4)

Copper sulfate g./l.	35
Nickel chloride g./l.	8
Formalin 37% solution ml./l.	100
Sodium hydroxide ml./l.	40
Thiourea ml./l.	0.001

Name	(5) Cahill's	(6) Cahill and McCornell's	(7) Suabestre's (1)	(8) Saubestre's (2)	(9) Godie's
Composition:					
Copper sulfate, g./l.	30	[1] 15	29	29	5
Sodium carbonate, g./l.	30	[2] 10	25	"	"
Potassium sodium tartrate, g./l.	100	30	140	140	25
Sodium hydroxide, g./l.	50	20	40	40	7
Formalin 37% solution, ml./l.	30	100	166	166	10
Versene T, g./l.*	"	"	17	"	"
pH	11.5	"	11.5	11.5	"
Temperature (° C.)	24	24	21	21	"

[1] Copper nitrate.
[2] Sodium bicarbonate.
*Mixture of EDTA and triethylamine at equal mol.

(10) Narcus's bath:

	G./l.
A solution:	
Copper sulfate	60
Nickel sulfate	16
Hydrazine sulfate	45
B solution:	
Sodium hydroxide	45
Potassium sodium tartrate	180
Sodium carbonate	15

Mixing A and B solution before using.

C. GOLD ELECTROLESS PLATING BATH

Potassium gold cyanide g./l.	2
Ammonium chloride g./l.	75
Sodium citrate g./l.	50
Sodium hypophosphite g./l.	10
pH (by NH_4OH)	7 to 7.5
Temperature ° C.	92 to 95

See also: nickel electroless plating bath:

(A)

(1) U.S. Pat. 2,940,018: composition of A. IV (1)
(2) U.S. Pat. 2,942,990: composition of A. II (1)
(3) M. Schwartz, "Proceeding American Electroplaters' Society," 47, 176 (1960): composition of A. IV. (2)
(4) E. B. Sanhestre, "Metal Finishing," 50 [6]67 (1962): composition of A. IV (3).

(B)

Copper electroless plating bath:

(1) W. Godie, "Plating," 51, 1069 (1964): composition of B.(9).
(2) Mccornell (U.S. Pat. 2,874,072): composition of B(6).

(C)

Gold electroless plating bath:

(1) S. D. Swan and E. L. Gostin, "Metal Finishing," 59, 4 (1961): composition of C.

The metal images produced by the present invention have many advantages. These advantages are as follows: (1) a high electric conductivity and a good thermal conductivity in the metal image area; (2) a high electric resistivity in the non-metal image area (background); (3) rapidness, that is, exposure is rapidly practiced and subsequent treatments are easily carried out; and (4) the metal image area is not injured and a circuit consisting of a narrow metal image area is not easily broken.

The present invention is useful for producing an electric circuit plate and can be used for the correction of circuit designs on circuit plates.

Further, the present invention can be utilized for producing a base plate of printing if the metal images are produced on a preferred hydrophilic surface. Hydrophilic surface used as follows:

(1) The surface of cellulose triacetate or cellulose diacetate is saponified to become hydrophilic.

(2) The surface of polystyrene is processed with chromic acid or corona discharge to make it hydrophilic.

(3) The surface of polyethylene terephthalate is processed with chromic acid to make hydrophilic.

Furthermore, the present invention can be utilized for producing a base plate for thermoprinting and thermocopying, if the metal images are produced on the surface of a plastic which is a thermal nonconductor.

As described above, the present invention has many industrial uses and many advantages. The metal images produced are very sharp and have a high electric conductivity and a good thermal conductivity.

The present invention will be explained in more detail by the following examples: (All thickness in the Examples are dry thickness.)

EXAMPLE 1

A cellulose triacetate film 135μ thick was dipped in a 1N aqueous solution of sodium hydroxide at 50° C. for 15 minutes, by which the surface was saponified to produce a hydrophilic surface part. The film was then dipped in a 0.1 mol aqueous solution of sodium sulfide at 25° C. for 15 minutes. After removing the solution on the surface by squeezing, the film was dipped in a 0.1 mol aqueous solution of nickel chloride at 25° C. for 3 minutes, followed by washing and drying. By these treatments, a sheet which contained nickel sulfide in a hydrophilic surface part as the diffusion transfer nucleus material was obtained. To this sheet, a silver chlorobromide emulsion (70% silver chloride) containing 1 mol of silver per kg. of the emulsion was applied so as to provide a 3μ thickness. The film was exposed to light through a positive original and then developed using a developer having the following composition at 25° C. for 30 seconds.

	G.
p-Methylaminophenol sulfate	5
Anhydrous sodium sulfite	65
Hydroquinone	15
Anhydrous sodium thiosulfate	15
Sodium hydroxide	20
Water to make 1 litre.	

The element was then dipped in warm water at 40° C. to remove the emulsion layer. At this stage, a positive image of the original formed on the element. The element was dipped in a 15% aqueous formalin solution for 8 minutes at 25° C. and then in a 0.8% aqueous palladium chloride solution having a pH of 2.0 for 60 seconds at 50° C. The element was then dipped in a Cahill's copper electroless plating at 24° C. for one minute, by which beautiful plating of copper was formed according to the pattern of the original. The electric conductiivty was below 0.2 Ω/square. Ω/square had a value of $\frac{1}{100}$ of the resistivity (Ω) of a resistance wire which had the length of 100 times the width thereof.

EXAMPLE 2

A cellulose triacetate film 135μ thick was dipped in a solution having the following composition at 20° C. for 3 minutes.

Sodium hydroxide g.	50
Ethyl alcohol ml.	500
Water ml.	500

The film was then dipped in a 0.1 mol aqueous solution of sodium sulfide. After removing the solution on the surface by squeezing, the film was dipped in a 0.1 mol aque-

ous solution of silver nitrate at 25° C. for 3 minutes, followed by washing and drying. By these treatments, a sheet which contained silver sulfide nuclei in a hydrophilic surface part was obtained.

To this sheet, a silver chlorobromide emulsion containing 1.2 mols of silver per kg. of the emulsion was applied to provide a 4μ thickness. The sheet was exposed to reflection rays using an original having a positive pattern of a circuit by means of a process camera at 16 of iris, 8 seconds, (diaphragm f:16, exposure time 8 seconds) and developed using a developer having the following composition at 20° C. for 20 seconds.

	G.
1-Phenyl-3-pyrazolidone	20
Anhydrous sodium sulfite	70
Hydroquinone	18
Anhydrous sodium thiosulfate	15
Potassium bromide	1.5
Sodium hydroxide	10
Water to make 1 litre.	

Upon removing the emulsion layer by spraying a jet of warm water at 40° C. thereon, a silver image was produced according to the positive original.

The resulting electric circuit consisting of the positive silver image was dipped into an aqueous solution of palladium chloride having an adjusted pH of 1.5 (palladium chloride content: 3.5%) at 30° C. for 40 seconds and then into a copper electroless solution (commercial name: Top Metalate Bath, produced by Okuno Seiyaku Co.) at 25° for 3 minutes to plate the silver image with copper. The electric conductivity of the circuit obtained by this process was below 0.1 Ω/square.

EXAMPLE 3

A sheet element having a 3-layer sandwiched structure was prepared by laminating a polyethylene of 30 g./m.² in weight with paper having a 100 g./m.² weight, and laminating the resulting paper with a cellulose acetate butyrate film 35μ thick (161–40, produced by Eastman Kodak Co.). This sheet element was dipped into a solution (prepared by dissolving 50 g. of sodium hydroxide in 500 ml. of methyl alcohol) at 35° C. for 2 minutes to saponify the surface of the cellulose.

The sheet element having a hydrophilic surface was dipped at 25° C. for 2 minutes into a solution prepared by dissolving 10 g. of silver nitrate in 500 ml. of water, adding 500 ml. of a 0.5 N sodium hydroxide solution thereto, and adding an aqueous ammonium solution till the produced silver oxide precipitate dissolved. Then the sheet element was dipped in a 3.7% aqueous formalin solution at 25° C. for 30 seconds, followed by squeezing and drying. By these treatments, a sheet element which contained colloidal silver in the part near the surface of the hydrophilic surface part was produced, the colloidal silver serving as the diffusion transfer nucleus material.

This sheet element was exposed to light through a positive original and developed by a developer having the composition of Example 1 at 25° C. for 30 seconds. By removing the emulsion layer by dipping in warm water at 50° C., silver images were produced according to the positive original. These were intensified with copper images by the electroless plating treatment of Example 1. The thus produced sheet element, in which the images were oleophilic and the surface part of the cellulose was hydrophilic, could be used as a lithographic offset printing plate. Using an available wetting solution and inks, more than 10,000 copies of printed material of good quality were obtained.

EXAMPLE 4

A polyethylene terephthalate film 135μ thick was treated by passage through a flame jet produced from propane gas and air so as to have a hydrophilic surface. [passing PET film base in the flame of propane gas and air running at 70 m./min., the surface is made oxidated and hydrophilic]. This film was dipped in a 0.2 mol aqueous solution of sodium sulfide at 40° C. for 10 minutes and then the solution on the surface was removed by squeezing. The film was then dipped in a 0.1 mol aqueous solution of nickel chloride at 25° C. for 3 minutes, followed by washing and drying. By these treatments, a polyethylene terephthalate film containing nickel sulfide as diffusion transfer nuclei was produced. To this sheet element, a silver bromoiodide emulsion containing 1.3 mols of silver per kg. of the emulsion (1.5% silver iodide) was applied to provide a 3μ thickness. The sheet element was exposed to light through a positive original and developed using a developer having the following composition at 25° C. for 45 seconds.

	G.
p-Methylaminophenol sulfate	5
Anhydrous sodium sulfite	70
Hydroquinone	15
Anhydrous sodium thiosulfate	18
Sodium hydroxide	20
Water to make 1 litre.	

The emulsion layer was removed by dipping in warm water at 45° C.

The element was then dipped into an aqueous formalin solution (25%) at 25° C. for 5 minutes, into a 3% aqueous solution of palladium chloride at 45° C. for 20 seconds and then into a copper electroless solution at 20° C. for 3 minutes to intensify the images with copper.

On the pattern of copper images formed on the sheets, a thermosensitive copying paper was laid. By uniformly applying infrared rays of an intensive luminous flux at the side of the polyethylene terephthalate film free of copper, a duplicated pattern was formed on the thermosensitive copying paper according to the metal images. Infrared ray was applied to the side free of copper. The infrared ray is absorbed in black image of silver and transmitted copper.

The copper electroless solution in Example 4 is as follows:

Copper sulfate 5 water	g./l.	29
Sodium carbonate	g./l.	25
Potassium sodium tartrate	g./l.	140
Sodium hydroxide	g./l.	40
Formation 37% solution	ml./l.	166

EXAMPLE 5

To a polyethylene terephthalate film support (thickness 135μ), a solution which contained 48 parts vinyl chloride (70 mol percent)-vinyl acetate (30 mol percent) copolymer and (polymerization degree is 400) 2.65 parts by weight of titanium dioxide pigment (based on parts by weight of the vinyl chloride-vinyl acetate copolymer) was applied so as to provide a 0.2 g./decimeter² thickness. A solution of this pigment in 52 parts methylethylketone was applied to the polyester support and dryed at 150° F. for 5 minutes. A composition containing finely-divided colloidal silica and colloidal silver having the following composition was applied to the resulting layer so as to provide a 1μ thickness.

	G.
Aqueous dispersion of colloidal silica having 30% by weight solids content	800
Secondary sulfate anionic surface active agent	4
Aqueous solution of colloidal silver (10% by weight) dispersed in casein (20%)	30

A silver chlorobromide photographic emulsion (silver chloride: 70%) was applied to the resulting silica layer.

This photographic image forming base plate was exposed by reflection rays to a positive original by means of a plate making camera at 16 of iris for 6 seconds. The plate was treated with using the same diffusion transfer developer as in Example 1 at 25° C. for 30 seconds.

Then the photographic emulsion layer was removed by warm water at 45° C. The silver images were intensified with metal images by electroless plating as described in Example 1. The metal images obtained had an excellent electrical conductivity which was below 1.5 Ω/square.

This invention is used to manufacture printed circuits, offset printing plates, master plates of heat-printing, master plates of heat duplicating, name plates, etc.

What is claimed is:

1. A process for producing metal images comprising image-exposing, through an original image, a photosensitive element which comprises a photosensitive silver halide photographic emulsion laid on a hydrophilic surface of a plastic which has a surface containing a diffusion transfer nucleus material, forming reversal silver images of the original on the surface of said plastic by a diffusion transfer developing process, removing said emulsion, activating said silver images with a solution of a metal salt, and intensifying said silver images by electrolessly plating a metal thereon.

2. A process for producing metal image as claimed in claim **1** wherein said metal image is nickel, copper, chrome, cobalt, silver or gold image.

3. A process for producing metal image as claimed in claim **1** wherein said silver halide is silver chloride, silver bromide, silver iodide, silver chlorobromide, silver bromoiodide, silver iodochloride, or silver chlorobromoiodide.

4. A process for producing metal image as claimed in claim **1** wherein said plastic is polyethylene terephthalate, polyvinylalcohol, cellulose triacetate, cellulose diacetate, cellulose propionate, cellulose butyrate, cellulose acetate propionate or cellulose acetate butyrate.

5. A process for producing metal images as claimed in claim **1** wherein said solution of metal salt is an aqueous solution of noble metal compound.

6. A process for producing metal images as claimed in claim **5** wherein said noble metal compound is selected from palladium (II) chloride, hydrogen gold (IV) chloride or diamine silver nitrate.

7. A process for producing metal images as claimed in claim **6** wherein said noble metal compound is palladium (II) chloride.

8. A process for producing metal images as claimed in claim **2** wherein said metal image is copper.

9. A process for producing metal images as claimed in claim **1**, wherein said plastic is a cellulose organic acid ester.

10. A process for producing metal images as claimed in claim **1** wherein said plastic is polyethylene-terephthalate.

11. A process for producing metal images as claimed in claim **1**, wherein said plastic is polyethylene.

12. A process for producing metal images as claimed in claim **9**, wherein said hydrophilic surface is obtained by contacting said cellulose organic acid ester with an aqueous solution of an alkali, a mixture of alkali-containing water and a solvent or an alkali-containing solvent.

13. A process for producing metal images as claimed in claim **10**, wherein said hydrophilic surface is obtained by a flame treatment.

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