Sept. 30, 1958 H. T. LYMAN ET AL 2,854,386

METHOD OF PHOTOGRAPHICALLY PRINTING CONDUCTIVE METALLIC PATTERNS

Filed Feb. 7, 1955

Fig. 1

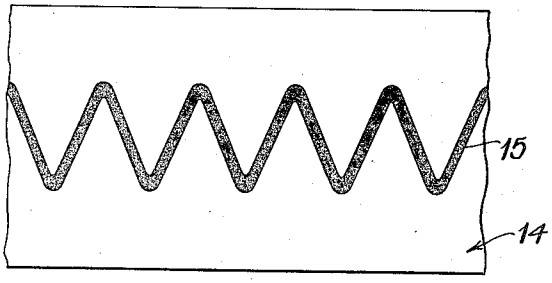


Fig. 2

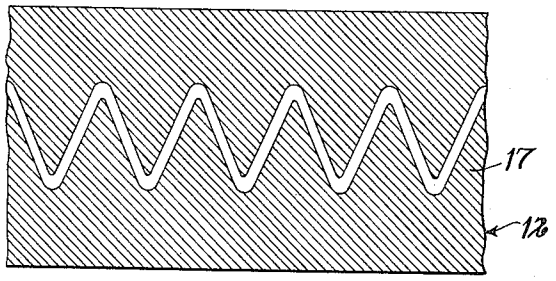


Fig. 3

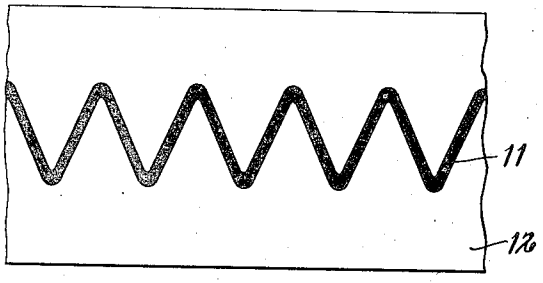


Fig. 4

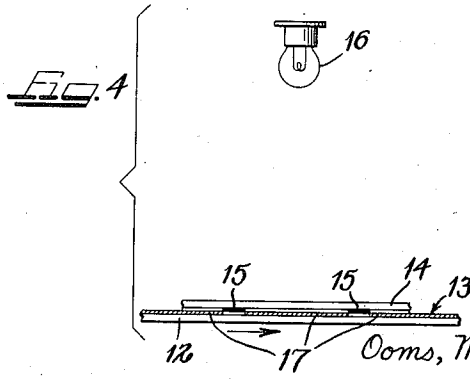


Fig. 5

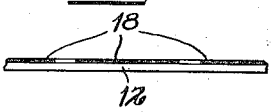


Fig. 6

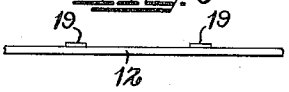


Fig. 7

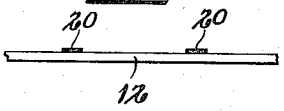
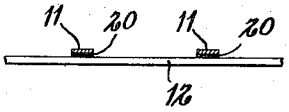


Fig. 8



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METHOD OF PHOTOGRAPHICALLY PRINTING CONDUCTIVE METALLIC PATTERNS

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13 Claims. (Cl. 204—15)

This invention relates to new and improved methods of photographically printing conductive metallic patterns, such as electrical circuits, coils, and other circuit elements, for example.

One principal object of the invention is to provide a new and improved photographic printing method whereby a continuously conductive metallic coating may be deposited on a support in any desired pattern.

A further object is to provide an improved direct metallizing process in which metal is deposited directly on photographically defined pattern areas of a support without depositing metal on the nonpattern areas.

Another object is to provide an improved metallizing process in which the need for recovery of metal from waste solutions is reduced to a minimum inasmuch as metal is deposited in the first instance only in desired pattern areas of a support.

It is a further object to provide an improved photographic metallizing process which will produce uniform, smooth, malleable continuously conductive coatings which are firmly adherent to a desired nonconductive support.

Further objects and advantages of the invention will appear from the following description of illustrative embodiments thereof, particularly when such description is taken with the accompanying drawings, in which:

Figure 1 is a plan view of a photographic transparency or master employed in one exemplary method embodying the invention;

Fig 2 is a plan view of a supporting sheet to be metallized by the exemplary method, the supporting sheet being shown at an intermediate stage in the method and with a negative photographic image of the desired metal pattern thereon;

Fig. 3 is a plan view of the supporting sheet with the final metal pattern thereon;

Fig. 4 is a diagrammatic cross-sectional view through the photographic transparency and the supporting sheet, to show the initial photographic printing of the emulsion coating on the sheet;

Fig. 5 is a digrammatic cross-sectional view showing the sheet after the first development of the emulsion;

Fig. 6 is a diagrammatic cross-sectional view showing the sheet after being subjected to an etching bath;

Fig. 7 is a diagrammatic cross-sectional view showing the sheet after re-exposure and redevelopment; and

Fig. 8 is a diagrammatic cross-sectional view showing the sheet with its final metallic pattern thereon.

The first exemplary method to be described is capable of forming a smooth malleable continuously conductive coating **11** in any desired pattern on an inert electrically nonconductive sheet **12** or other support. As shown, the support **12** is in the form of a thin flexible strip of plastic film, but it may be in any desired form and may be made of any suitable material, such as various plastics or glass, for example.

In the present exemplary method, the support **12** is provided initially with a thin photographically sensitive

coating **13** comprising a gelatin emulsion containing light sensitive silver bromide or other silver halide. It is preferred to employ a minimum thickness of hard tough gelatin, firmly bonded to the support **12**. Where the support **12** may be in the form of a thin flexible film, as in the present case, the support and its emulsion may take the form of various commercially available brands of photographic film, such as DuPont Positive Micro-film, Kodak Positive Print Film, Kodak Kodalith Film, or Ansco Reprolith Film, for example.

Although metal may be deposited on the support **12** in any desired pattern, it will be assumed, by way of example, that the final coating **11** is to be in the form of a zig-zag ribbon or strip, which may be considered to be the conductor of an inductance coil or other circuit element.

The zig-zag pattern is printed photographically on the photographically sensitive support **12** with the aid of a master transparency **14** (Fig. 1) bearing an image **15** of the desired pattern. Preferably, the transparency **14** constitutes a photograph of the desired pattern, although it may comprise a drawing or any other reproduction thereof. In the particular method being described, the pattern image **15** is made relatively opaque while the remainder of the master **14** is made transparent. It will be seen that the master **14** is in the form of a thin flexible strip of photographic film.

Any standard or suitable photographic printing technique may be employed to expose the emulsion **13** on the support **12** to a light image of the pattern **15** on the master **14**. As shown diagrammatically in Fig. 4, it is preferred to employ contact printing, in which the master **14** is maintained in contact with the emulsion coated support **12**, while actinic radiation from a light source **16** is directed through the master **14** onto the emulsion **13**. In the light image thus formed on the emulsion **13**, the nonpattern areas are illuminated while the pattern areas are left substantially unilluminated. In the printing operation the master **14** and the support **12** are preferably moved continuously past the light source **16** so that any desired length of the emulsion coated support **12** may be printed in one continuous operation. Any known or suitable continuous printer may be employed. The light source **16** may be a standard incandescent lamp supplied from a variable voltage source to regulate the exposure given to the emulsion **13**.

It will be understood that the illumination of the nonpattern areas of the emulsion **13** forms a latent silver image **17** therein, by partial reduction of the silver halide in the emulsion. The latent image **17** is negative or reversed relative to the final pattern **11**.

The latent image **17** is developed into a dense and visible silver image **18** (Fig. 5) by means of a standard or suitable developer bath capable of selectively reducing the silver halide in the exposed areas of the emulsion **13**. It is preferable to employ a high-contrast, nonfogging developer, which cuts off development very sharply in the low densities. One suitable standard developer is Eastman Kodak developer D–85, having the following formula:

Water	cc	500
Sodium sulfite	grams	30.0
Paraformaldehyde	do	7.5
Sodium bisulfite	do	2.2
Boric acid (crystal)	do	7.5
Hydroquinone	do	22.5
Potassium bromide	do	1.6

Water to make 1.0 liter.

The development may proceed for about three minutes at 68 degrees F., whereupon the emulsion **13** with its

support **12** is transferred to an acid stop bath and agitated about fifteen seconds. The stop bath may comprise a three percent solution of acetic acid in water.

As will soon become clearly apparent, the initial development has the effect of conditioning the emulsion **13** for selective removal of the gelatin from the nonpattern areas in a suitable solvent, while leaving the gelatin in the pattern areas. The preferred solvent is a silver oxidizing etch bath which attacks the metallic silver in the image **18** and simultaneously softens the associated gelatin and loosens it from the support **12**. One suitable etch bath is the standard Eastman Kodak Etch Bath EB–2, which has the following formula:

Solution A

Water	cc	750
Copper sulfate	grams	120.0
Citric acid	do	150.0
Potassium bromide	do	7.5

Water to make 1000 cc.

Solution B

Hydrogen peroxide—3% solution in water

For use, mix equal parts of solutions A and B.

The emulsion **13** and its support **12** is subjected to the etch bath with constant agitation until the silver image **18** is completely bleached through, whereupon it will be found that the associated gelatin has separated from the supporting base **12**, leaving the emulsion intact, however, in the unexposed pattern areas, to form a gelatin image **19** (Fig. 6). The loosened gelatin may be removed by gently swabbing the support **12** with wet cotton, without applying any substantial pressure. Then the support **12** is rinsed under a gentle stream of water.

As the next step, a preliminary or latent silver deposit is formed in the gelatin image **19**, preferably by re-exposing the whole support **12** to a strong light source, such as an incandescent lamp. This exposure to light partially reduces the silver halide remaining in the gelatin image **19**.

The silver particles in the preliminary deposit serve as "seeds" or nuclei for the formation of a heavy, continuously conductive silver deposit **20** which impregnates and covers the gelatin image **19**. To form the heavy deposit **20**, the re-exposed support **12** is subjected to redevelopment in a physical developer bath containing a reducing agent and a silver salt. The reducing agent reduces the silver halide in the gelatin image **19** to metallic silver and, at the same time, reduces the silver salt in the developer, with the result that additional silver is deposited in and on the gelatin image **19** by the developer. This additional silver strongly adheres to the silver-bearing gelatin image.

A physical developer having the following formula has been successfully employed and is preferred in the exemplary method:

Solution A

Water	cc	3000
Glycin	grams	8
Phenol p-methylamino sulfate	do	20
Sodium sulfite	do	400
Sodium thiocyanate	do	6

Water to make 4000 cc.

Solution B

Silver nitrate—1% solution in water

For use, mix one part of solution B with ten parts of solution A, measured by volume.

It has been found that the gelatin image **19** may be metallized in about twenty-five minutes in this physical developing bath. Next, it is generally desirable that the supporting film **12**, with its silvered gelatin pattern, be washed, dried, and film **12** is buffed gently with a fibrous pad, to remove any silver sediment or precipitate from the film base, while polishing the silver deposit **20**, which remains adherent to the gelatin image **19**. Any silver precipitated on the support **12** is not adherent thereto and is easily removed. It has been found that the buffing operation increases the conductivity of the silver pattern **20**. However, in some cases the film base is so clean and free of sediment that buffing is not necessary and may be omitted.

The silver pattern **20** is continuously conductive to electricity and hence may be coated with copper or some other metal by standard electroplating techniques. It is preferred to electroplate copper onto the silver pattern **20** by using an acid copper electroplating bath, which may have the following composition:

Water	liters	9
Copper sulfate	grams	250
Sulfuric acid	cc	15–30
Thiourea	grams	0.005–0.01

Electroplating the silver pattern **20** results in the final copper pattern **11**, which is adequately smooth, bright and malleable and is strongly adherent to the support **12**.

In this method, the provision of an initial gelatin emulsion **13** which is tough, hard and of minimum thickness contributes to the smoothness, softness and malleability of the final metal pattern. With such an initial tough, thin emulsion, there is no excess, spongy gelatin to interfere with maintaining the conductivity of the metallized image, or to contaminate the acid copper plating solution. Moreover, the finished metal pattern is firmly adherent to the supporting base.

While the above described method is preferred and has given the best results, it is possible to modify the method in various ways, while retaining satisfactory results. In one modified method the support to which the metal pattern is to be applied is provided with a standard or suitable "wash off" type of emulsion coating, composed of soft unhardened gelatin, containing a light sensitive tanning agent such as potassium bichromate, for example. Where the support can be thin and flexible, it may take the form of various commercial brands of photographic film, such as Kodak Ektagraph film.

The desired pattern is selected and is photographed to produce a negative master, in which the pattern areas are transparent and the nonpattern areas are opaque. Actinic illumination is directed through the master to form a light image on the wash-off emulsion. It will be understood that the desired pattern areas are exposed to the illumination while the nonpattern areas are not. In order to actuate the tanning agent with maximum speed, it is preferred to employ contact printing with ultraviolet illumination, directed first through the master and then through the supporting film base onto the underside of the emulsion. In the illuminated pattern areas, the tanning agent is activated so that it hardens the gelatin. Because the light is directed through the film base, the underside of the emulsion is hardened to the greatest extent.

After exposure, the emulsion is subjected to an alkaline activator or developer bath containing a gelatin swelling agent, such as sodium hydroxide, for example. In the unexposed nonpattern areas, the gelatin becomes swollen and relatively soluble in warm water, while the tanned gelatin in the pattern areas remains relatively unswollen and insoluble.

Next, the supporting film and its wash-off emulsion is immersed in warm water at about 100 degrees to 120 degrees F. and then is washed in a spray of warm water at the same temperature to dissolve or soften the gelatin in the nonpattern areas. The spray completely removes the unexposed emulsion while leaving the exposed emulsion intact on the supporting film, to form a gelatin image of the desired pattern.

As in the first method, a preliminary silver image or deposit is formed in the gelatin image, but this is done in a different manner. First, the supporting film with its gelatin image is immersed in an alkaline bath constitut-

ing a solution of an alkali metal hydroxide. A one percent solution of sodium hydroxide is preferred. After the hydroxide has penetrated the gelatin, the film is transferred momentarily to a water wash bath and then to a bath containing a silver salt. For the latter bath a one percent solution of silver nitrate is preferred. In some cases ammonium hydroxide has been added to the silver nitrate bath until the initial precipitate has been redissolved. The silver nitrate reacts with the sodium hydroxide in the gelatin image to form a deposit of silver oxide.

For best results, the supporting film is alternated several times between the hydroxide and silver baths, with brief rinsing therebetween. Three or four cycles have been found sufficient to build up an adequate deposit of silver oxide in the gelatin image. In each cycle, the film may remain in the hydroxide bath for about two minutes, and in the silver bath until the reaction is apparently completed. After several cycles, the gelatin image will be coated with a dull dichroic silvery luster.

As an optional next step, the film may be immersed in a .01 percent solution of Hydrazine Sulfate, but this is not necessary.

As in the first exemplary method, the supporting film is next redeveloped in a physical developer to reduce the silver oxide and deposit additional silver to form a continuously conductive coating. The same physical developer may be used as in the first described method.

After thorough rinsing, the film is dried and buffed briskly with soft cotton or other fibrous material, as in the first method. The buffing removes any sediment from the film base and polishes the silver coated gelatin image to increase its conductivity.

The conductivity of the silvered image may be further increased by adding a deposit of copper or other metal. Copper may be added by immersing the film in a solution of copper sulfate and then dusting the film with iron powder. The result is the deposition of a bright film of metallic copper on the silvered image. Agitation of the film during this step is important to prevent the deposition of a dull brown film of copper oxide. It will be understood that the copper is displaced from the solution by the iron and is selectively deposited on the silvered image. The copper does not adhere to the film base.

As an alternative method of depositing copper on the silvered gelatin image, the film may be immersed in a copper sulfate solution containing sodium hydroxide, Rochelle salts, and formaldehyde. Again, the copper is reduced and is deposited as a bright film on the silvered image.

The conductivity of the coppered image may be increased still further by passing the film through an immersion silvering bath, which may comprise a solution of silver nitrate, ammonium hydroxide, and sodium thiosulfate. In this bath, a film of silver is deposited on the copper coated image.

After rinsing, the film may be returned to the copper depositing bath. Several cycles of alternate coppering and silvering may be employed, if desired. A final coating of copper may be added by electroplating in a standard acid copper plating bath. With this step the metal pattern is complete.

The modified or second described method may be modified still further by employing a support having a wash-off gelatin emulsion containing a silver halide as a light sensitizing agent, rather than a bichromate or other tanning agent. Such silver halide-gelatin wash-off emulsions are available commercially on flexible film bases. One such film is Kodak Matrix Film.

Such a silver halide gelatin wash-off emulsion is relatively sensitive and may be exposed with ordinary incandescent illumination. Otherwise, the exposure of the film is the same as in the second method.

The film is developed in any standard or suitable selective hardening developer, which contains an agent or agents capable of reducing the silver halide in the exposed pattern areas of the emulsion and simultaneously hardening the surrounding gelatin. One such developing agent is the well known pyrogallic acid. After such development, the gelatin in the pattern areas is relatively insoluble in warm water, while the unhardened gelatin in the nonpattern areas remains relatively soluble. As in the second described method, the gelatin in the nonpattern areas may be removed with warm water. All further processing of the film may be the same as in the second method.

It will be understood that any suitable nonconductive inert support may be employed in any of the exemplary methods, simply by applying the appropriate light sensitive emulsion to the selected support and otherwise carrying out the method as described.

The exemplary methods are essentially additive rather than subtractive, in the sense that the desired pattern is formed by depositing metal where desired, rather than removing metal from a complete coating where not desired. Accordingly, the need for recovering metal from waste solutions is minimized. Thus the methods of this invention are highly economical.

Various other modifications, equivalents, and alternative methods may be employed, without departing from the true spirit and scope of the invention as exemplified in the foregoing description and defined in the following claims.

We claim:

1. A method of photographically forming a conductive metallic pattern, said method comprising providing an electrically insulating chemically inert support having a coating thereon of a light sensitive emulsion of gelatin and a silver halide, exposing a first area of said coating to light while leaving a second area of said coating substantially unexposed, said second area corresponding in shape to the desired pattern, all of said coating thereby being exposed to light except for said second area, a latent silver image thereby being formed in said first area, developing said latent image with a silver halide reducing developer to form a visible silver image in said first area, etching said visible silver image with a silver etching bath and thereby selectively loosening the gelatin emulsion from said support in said first area, washing away the loosened gelatin emulsion in said first area, illuminating the emulsion remaining in said second area to form a latent silver pattern image, redeveloping said remaining emulsion with a silver depositing physical developer containing a silver salt and a reducing agent therefor and thereby forming a substantially continuous coating of silver on said remaining emulsion in said pattern areas, drying said support and emulsion, buffing said support and emulsion with a soft fibrous material to remove any silver precipitate from said support and to polish said silver coating, said coating being continuously electrically conductive, and applying additional metal to said coating by electroplating.

2. A method of photographically forming a conductive metallic pattern, said method comprising providing an electrically insulating chemically inert support having a coating thereon of a light sensitive emulsion of gelatin and a silver halide, exposing a first area of said coating to light while leaving a second area of said coating substantially unexposed, said second area corresponding in shape to the desired pattern, all of said coating thereby being exposed to light except for said second area, a latent silver image thereby being formed in said first area, developing said latent image with a silver halide reducing developer to form a visible silver image in said first area, etching said visible silver image with a silver etching bath containing hydrogen peroxide and thereby selectively loosening the gelatin emulsion from said support in said first area, washing away the loosened gelatin emulsion in said first area, illuminating the emulsion

remaining in said second area to form a latent silver pattern image, redeveloping said remaining emulsion with a silver depositing physical developer containing a silver salt and a reducing agent therefor and thereby forming a substantially continuous coating of silver on said remaining emulsion in said second area, drying said support and emulsion, buffing said support and emulsion with a soft fibrous material to remove any silver precipitate from said support and to polish said silver coating, said coating being continuously electrically conductive, and applying additional metal to said coating by electroplating.

3. A method of photographically forming a conductive metallic pattern, said method comprising providing an electrically insulating chemically inert support having a coating thereon of a light sensitive emulsion of gelatin and a silver halide, exposing a first area of said coating to light while leaving a second area of said coating substantially unexposed, said second area corresponding in shape to the desired pattern, all of said coating thereby being exposed to light except for said second area, a latent silver image thereby being formed in said first area, developing said latent image with a silver halide reducing developer to form a visible silver image in said first area, etching said visible silver image with a silver etching bath and thereby selectively loosening the gelatin emulsion from said support in said first area, washing away the loosened gelatin emulsion in said first area, illuminating the emulsion remaining in said second area to form a latent silver pattern image, redeveloping said remaining emulsion with a silver depositing physical developer containing silver nitrate and a reducing agent therefor and thereby forming a substantially continuous coating of silver on said remaining emulsion in said second area, drying said support and emulsion, buffing said support and emulsion with a soft fibrous material to remove any silver precipitate from said support and to polish said silver coating, said coating being continuously electrically conductive, and applying additional metal to said coating by electroplating.

4. A method of photographically forming a conductive metallic pattern, said method comprising providing an electrically insulating chemically inert support having a coating thereon of a light sensitive emulsion of gelatin and a silver halide, exposing a first area of said coating to light while leaving a second area of said coating substantially unexposed, said second area corresponding in shape to the desired pattern, all of said coating thereby being exposed to light except for said second area, a latent silver image thereby being formed in said first area, developing said latent image with a silver halide reducing developer to form a visible silver image in said first area, etching said visible silver image with a silver etching bath and thereby selectively loosening the gelatin emulsion from said support in said first area, washing away the loosened gelatin emulsion in said first area, illuminating the emulsion remaining in said second area to form a latent silver pattern image, redeveloping said remaining emulsion with a silver depositing physical developer containing a silver salt and a reducing agent therefor and thereby forming a substantially continuous coating of silver on said remaining emulsion in said second area, drying said support and emulsion, buffing said support and emulsion with a soft fibrous material to remove any silver precipitate from said support and to polish said silver coating, said coating being continuously electrically conductive, and applying additional metal to said coating by electroplating copper thereon in an acid copper electroplating bath.

5. A method of photographically forming a conductive metallic pattern, said method comprising providing an electrically insulating chemically inert support having a coating thereon of a light sensitive emulsion of gelatin and a silver halide, exposing a first area of said coating to light while leaving a second area of said coating substantially unexposed, said second area corresponding in shape to the desired pattern, all of said coating thereby being exposed to light except for said second area, a latent silver image thereby being formed in said first area, developing said latent image with a silver halide reducing developer to form a visible silver image in said first area, etching said visible silver image with a silver etching bath containing hydrogen peroxide and thereby selectively loosening the gelatin emulsion from said support in said first area, washing away the loosened gelatin emulsion in said first area, illuminating the emulsion remaining in said second area to form a latent silver pattern image, redeveloping said remaining emulsion with a silver depositing physical developer containing silver nitrate and a reducing agent therefor and thereby forming a substantially continuous coating of silver on said remaining emulsion in said second area, drying said support and emulsion, buffing said support and emulsion with a soft fibrous material to remove any silver precipitate from said support and to polish said silver coating, said coating being continuously electrically conductive, and applying additional metal to said coating by electroplating copper thereon in an acid copper electroplating bath.

6. A method of photographically forming a conductive metallic pattern, said method comprising providing an inert support having a light sensitive gelatin emulsion coating, selectively exposing said coating to light with an image composed of a first area and a second area, one of said areas being illuminated and the other of said areas being substantially unilluminated, said second area corresponding in shape to the desired pattern, developing said emulsion with a bath for rendering said first area relatively more susceptible than said second area to a predetermined solvent, removing the gelatin emulsion from said support in said first area with said predetermined solvent while leaving the gelatin on said support in said second area, forming a preliminary silver image in said emulsion in said second area, redeveloping said emulsion with a silver depositing physical developer containing a silver salt and a reducing agent therefor and thereby forming a substantially continuous coating of silver on said emulsion in said second area, drying said support and emulsion, and buffing said support and emulsion to remove any silver precipitate from said support and to polish said silver coating.

7. A method of photographically forming a conductive metallic pattern, said method comprising providing an inert support having a light sensitive soft gelatin emulsion coating, selectively exposing said coating to light with an image composed of a first area and a second area, one of said areas being illuminated and the other of said areas being substantially unilluminated, said second area corresponding in shape to the desired pattern, developing said emulsion with a bath for rendering said first area relatively more susceptible than said second area to removal by warm water, removing the gelatin emulsion from said support in said first area with warm water while leaving the gelatin on said support in said second area, forming a preliminary silver image in said emulsion in said second area, redeveloping said emulsion with a silver depositing physical developer containing a silver salt and a reducing agent therefor and thereby forming a substantially continuous coating of silver on said emulsion in said second area, drying said support and emulsion, and buffing said support and emulsion to remove any silver precipitate from said support and to polish said silver coating.

8. A method of photographically forming a conductive metallic pattern, said method comprising providing an inert support having a light sensitive silver halide bearing soft gelatin emulsion coating, selectively exposing said coating to light with an image composed of a first area and a second area, one of said areas being illuminated and the other of said areas being substantially unilluminated, said second area corresponding in shape to the desired pattern, developing said emulsion with a silver halide

reducing gelatin tanning developer bath for rendering the gelatin in said second area harder and less susceptible to removal by warm water than in said first area, removing the gelatin emulsion from said support in said first area with warm water while leaving the gelatin on said support in said second area, forming a preliminary silver image in said emulsion in said second area, redeveloping said emulsion with a silver depositing physical developer containing a silver salt and a reducing agent therefor and thereby forming a substantially continuous coating of silver on said emulsion in said second area, drying said support and emulsion, and buffing said support and emulsion to remove any silver precipitate from said support and to polish said silver coating.

9. A method of photographically forming a conductive metallic pattern, said method comprising providing an inert support having a soft gelatin emulsion coating containing a light sensitive gelatin tanning agent, selectively exposing said coating to light with an image composed of a first area and a second area, one of said areas being illuminated and the other of said areas being substantially unilluminated, said second area corresponding in shape to the desired pattern, developing said emulsion with an alkaline bath for rendering said first area relatively more susceptible than said second area to removal by warm water, removing the gelatin emulsion from said support in said first area with hot water while leaving the gelatin on said support in said second area, forming a preliminary silver image in said emulsion in said second area by alternately subjecting said emulsion to a first bath containing an alkali metal hydroxide and a second bath containing a silver salt, redeveloping said emulsion with a silver depositing physical developer containing a silver salt and a reducing agent therefor and thereby forming a substantially continuous coating of silver on said emulsion in said second area, drying said support and emulsion, and buffing said support and emulsion to remove any silver precipitate from said support and to polish said silver coating.

10. A method of photographically forming a conductive metallic pattern, said method comprising providing an inert support having a gelatin emulsion coating containing a light sensitive silver halide, exposing a first area of said coating to light while leaving a second area of said coating substantially unexposed, said second area corresponding in shape to the desired pattern, all of said coating thereby being exposed to light except for said second area, developing said emulsion with a silver halide reducing developer bath and thereby forming a silver deposit in said first area to render said first area susceptible to attack by a silver oxidizing gelatin removing etch bath, removing the gelatin emulsion from said support in said first area with a silver oxidizing gelatin removing etch bath while leaving the gelatin on said support in said second, forming a preliminary silver image in said emulsion on said second area by exposing said emulsion to light, redeveloping said emulsion with a silver depositing physical developer containing a silver salt and a reducing agent therefor and thereby forming a substantially continuous coating of silver on said emulsion in said second area, drying said support and emulsion, and buffing said support and emulsion to remove any silver precipitate from said support and to polish said silver coating.

11. A method of photographically forming a conductive metallic pattern, said method comprising providing an electrically insulating chemically inert support having a coating thereon of a light sensitive emulsion of gelatin and a silver halide, exposing a first area of said coating to light while leaving a second area of said coating substantially unexposed, said second area corresponding in shape to the desired pattern, all of said coating thereby being exposed to light except for said second area, a latent silver image thereby being formed in said first area, developing said latent image with a silver halide reducing developer to form a visible silver image in said first area, etching said visible silver image with a silver etching bath and thereby selectively loosening the gelatin emulsion from said support in said first area, washing away the loosened gelatin emulsion in said first area, illuminating the emulsion remaining in said second area to form a latent silver pattern image, and redeveloping said remaining emulsion with a silver depositing physical developer containing a silver salt and a reducing agent therefor and thereby forming a substantially continuous coating of silver on said remaining emulsion in said second area.

12. A method of photographically forming a conductive metallic pattern, said method comprising providing an inert support having a light sensitive gelatin emulsion coating, selectively exposing said coating to light with an image composed of a first area and a second area, one of said areas being illuminated and the other of said areas being substantially unilluminated, said second area corresponding in shape to the desired pattern, developing said emulsion with a bath for rendering said first area relatively more susceptible than said second area to a predetermined solvent, removing the gelatin emulsion from said support in said first area with said predetermined solvent while leaving the gelatin on said support in said second area, forming a preliminary silver image in said emulsion in said second area, and redeveloping said emulsion with a silver depositing physical developer containing a silver salt and a reducing agent therefor and thereby forming a substantially continuous conductive coating of silver on said emulsion in said second area.

13. A method of photographically forming a conductive metallic pattern, said method comprising providing an inert support having a light sensitive soft gelatin emulsion coating, selectively exposing said coating to light with an image composed of a first area and a second area, said second area being illuminated and said first area being substantially unilluminated, said second area corresponding in shape to the desired pattern, developing said emulsion with a bath for rendering said first area relatively more susceptible than said second area to removal by warm water, removing the gelatin emulsion from said support in said first area with warm water while leaving the gelatin on said support in said second area, forming a preliminary silver image in said emulsion in said second area, and redeveloping said emulsion with a silver depositing physical developer containing a silver salt and a reducing agent therefor and thereby forming a substantially continuous coating of silver on said emulsion in said second area.

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CERTIFICATE OF CORRECTION

Patent No. 2,854,386 September 30, 1958

Harold T. Lyman et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 9, line 55, for "second," read -- second area, --.

Signed and sealed this 9th day of December 1958.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents