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3,625,687

PROCESS FOR MAKING NEGATIVE WORKING OFFSET MASTERS CONTAINING THIN GELA- TIN RELIEF IMAGES

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13 Claims

ABSTRACT OF THE DISCLOSURE

Process for making a planographic printing master which comprises (a) exposing the silver halide emulsion layer of a photographic film, (b) developing the layer to form reduced silver images in the exposed areas, (c) simultaneously or sequentially with (b) developing the layer by silver transfer development to form a silver surface image in the unexposed areas, (d) treating the developed layer with an acidic peroxide etch-bleach solution, and (e) removing the degraded colloid binder to uncover an oleophilic surface in the exposed areas and leave an oleophobic surface in unexposed areas.

This invention relates to a photolithographic process. Specifically this invention relates to a process for the preparation of lithographic printing plates from photographic films bearing a silver halide emulsion layer.

The use of acid-hydrogen peroxide solutions containing heavy metal and halide ions to etch developed photographic emulsions is old in the art. In U.S. Pat. No. 2,013,116 a printing plate is obtained by hardening the emulsion, exposing, developing, and softening the exposed portions with a hydrogen peroxide, potassium bromide solution. The ink prints from the hardened, unexposed portions of the emulsion. According to U.S. Pat. No. 2,058,396 a printing plate is obtained by exposing an emulsion, developing, etching out the exposed portions with a hydrogen peroxide, nitric acid, copper sulfate and potassium bromide solution, developing with a tanning developer, and bleaching with a tanning bleach bath.

As used in the description of this invention, an oleophilic surface is a surface which accepts greasy ink and a hydrophilic surface is a surface which accepts water. A positive oleophilic image is one in which the oleophilic areas correspond to the black areas of the original and the areas corresponding to the clear areas of the original are hydrophilic and oleophobic. A lithographic plate having a negative oleophilic image is defined as a "negative-working" plate. A "negative" copy is defined as a copy obtained from a negative-working plate. Such plates may be mounted on a roller of an offset printing press, for example, and passed in contact with an aqueous fountain solution and a printing ink. The inked image is then applied to the sheet to be printed.

The term "nucleating agent" means an agent which acts as development nuclei of sufficient size to catalyze the silver reduction reaction whereby a negative silver image develops in a previously exposed, light-sensitive emulsion layer and the undeveloped silver grains dissolve, diffuse, and plate out as an inverse or positive image on the nuclei when the product is developed in a developer containing a silver halide solvent.

The making of superior planographic printing plates requires a delicate balance of a variety of characteristics of the coating, some of which tend to conflict with others. The coating must accept and retain a greasy image only in the desired areas when an aqueous fountain solution is used. The coating must permit the making of erasures, when necessary, without causing "halos" or other unde-

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sirable images to appear. The image must remain sharp throughout prolonged use, and not "tone." "Stop-go" characteristics, that is, the ability to print satisfactory copies after a period of machine shutdown, must also be good. These and other characteristics must be properly balanced to provide a superior plate, due regard being had for ease of manufacture and over-all cost.

The novel process of this invention, which fulfills these preferred printing characteristics, in its broader aspect comprises:

(a) Exposing a light-sensitive colloid silver halide emulsion layer of a photographic film having a flexible film base,

(b) Developing the exposed silver halide areas of said layer,

(c) Developing the unexposed areas of said layer with a silver transfer developer solution either sequentially or simultaneously with step (b),

(d) Bleaching the developed layer resulting from steps (b) and (c) with a gelatin-degrading aqueous acidic peroxide bleaching solution, and

(e) Removing the degraded colloid binder and material associated therewith to uncover the oleophilic surface of said film base in the exposed areas and leaving an oleophobic water-permeable colloid-containing surface in the unexposed areas of said layer.

In those cases where the etching is complete or down to the surface of the film base, the surface must be oleophilic, but, if there is an oleophilic coating on the film base, bleaching is required only to the surface of the coating. In the latter case, the base film may be either oleophilic or hydrophilic.

In the process, the silver halide emulsion layer may be outermost, in which case the silver surface image is present on and/or near the surface of such layer. However, if a colloid antiabrasion layer is present, the silver surface image will be formed in that layer.

During development with a silver transfer developer solution, it is believed that the silver ions migrate to or near the surface of the light-sensitive element as a complex ion. The nucleating agents, having permeated the surface region, are the starting points for reduction of the silver ion complex to metallic silver.

When practicing a preferred embodiment of this invention, an orthochromatically sensitized, lithographic, gelatino-silver halide emulsion is coated on an oleophilic/hydrophobic support preferably polyethylene terephthalate having an oleophilic copolymer coating, exposed to actinic radiation and then silver transfer developed. The developer is a super-additive developer containing a silver halide solvent such as sodium thiosulfate or potassium thiocyanate in amounts of 5 g. to 150 g. per liter of developer and a nucleating agent such as 0.1 M to 0.001 M sodium sulfide. During silver transfer development a black silver image is formed in the exposed areas, while in the unexposed areas, the undeveloped silver halide dissolves and diffuses as a silver complex to the sulfide nuclei where it reduces to form a positive, mirror like, surface, silver image covering the unexposed areas. After silver transfer development, the photosensitive film may be immersed in a conventional short stop solution, usually 1% to 5% acetic acid. The film is then immersed in or treated with a bleach-etch solution comprising a halide, usually potassium bromide, in amounts of 0.1 g./l. to 10 g./l., a heavy metal salt, e.g., cupric nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) in amount of 0.5 g./l. to 70 g./l., an acid, e.g., lactic acid (85%) in amounts 1 ml./l. to 100 ml./l., and hydrogen peroxide in concentrations of 0.1% to 3%. During the bleaching and etching step, the silver and gelatin in the exposed areas and the top layer of transfer developed silver and gelatin in the unexposed areas will be removed

leaving a low gelatin relief image. The process of bleaching and etching in the exposed areas is different than that in the silver transfer developed areas because of the concentration of silver in the silver image. In the unexposed areas, the developed silver is concentrated near the surface while in the exposed areas, developed silver is dispersed throughout.

Consequently, only partial etching occurs in the unexposed areas while total etching occurs in the exposed areas. The overall etching rate also depends upon the concentrations of the elements of the etching solution, temperature and agitation. Thus, when the film is removed from the etching solution, the surface is rubbed lightly whereby any remaining exposed areas are removed to the oleophilic surface, while in the silver transfer developed areas, the surface image only is removed leaving a thin, oleophobic, gelatin relief beneath the surface image. This gelatin relief may be treated with a gelatin hardener, e.g., glyoxal in amounts of 10 ml. to 100 ml. per liter of water. This treatment will extend plate life during printing. The plate may be mounted on an offset printing press, fountain solution such as gum arabic and asphaltum applied, and the plate inked, and a large number of printed copies having sharp images will be produced.

The following examples will further illustrate this invention but are not intended to limit the scope of this invention. The solutions are aqueous unless stated otherwise.

EXAMPLE I

A 0.004-inch thick polyethylene terephthalate film having a resin-subbing layer of vinylidene chloride/methyl acrylate/itaconic acid copolymer as described in Example IV, U.S. Pat. 2,779,684, was overcoated with a gelatin subbing layer. On this base there was coated an orthochromatically sensitized emulsion containing 20 mole percent silver bromide, 80 mole percent silver chloride, and 110 grams of gelatin per mole of silver halide. A conventional antiabrasion layer of clear, hardened gelatin containing silica particles was coated over the emulsion layer.

The light-sensitive element was exposed at a distance of two feet for 20 seconds to a high intensity-tungsten filament incandescent lamp, e.g., No. 2 General Electric Photoflood lamp operated at 17 volts. Exposure was to a positive having a density of 1.4.

A developer solution, Solution A, was prepared as follows:

Solution A

Water—600 ml.
Sodium sulfite (anhydrous)—33.3 g.
Hydroquinone (anhydrous)—10 g.
1-phenyl-3-pyrazolidone (reagent grade)—1 g.
Ethylene glycol—66.7 ml.
N-methyl-2-pyrrolidone—3.3 g.
Potassium carbonate (anhydrous)—26.6 g.
Benzotriazole—0.5 g.
Sodium hydroxide (13 grams dissolved in sufficient water to make 100 ml. of solution)—100 ml.
Trisodium salt of ethylenediamine tetraacetic acid—0.15 g.
Thiourea (0.1 M)—25 ml.
Potassium thiocyanate (reagent grade)—20 g.
Water to make 1 liter.

The exposed film immersed for one minute in Solution A and then washed with water for three minutes. The undeveloped silver halide in the unexposed areas dissolved and diffused as a silver complex to the receptive nuclei, the thiourea at or near the surface of the antiabrasion layer, where it was reduced to form a positive, mirror-like, surface, silver image whose surface was oleophilic relative to the surface of the exposed areas. A conventional black silver image formed in the exposed areas.

Solution B, a bleach-etch solution, was prepared as follows:

Solution B

5 Cupric nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$)—18.8 g.
Potassium bromide—1.0 g.
Lactic acid (85%)—15.6 ml.
Hydrogen peroxide (3%)—250 ml.
Water to make 1 liter

10 The developed film was placed in Solution B for three minutes. The etched film was then sponged and washed under running water until the exposed regions and the silver transfer developed silver surface image was removed. In the exposed areas, etching was complete, down to the oleophilic surface of the base while in the silver transferred, unexposed areas, etching was sufficient to remove only the positive silver surface image. By this process, a hydrophilic gelatin relief image was obtained in the unexposed areas thus producing a negative-working lithographic plate. Prior to inking and use as a printing plate, the plate was wetted with a five percent acetic acid solution. A conventional greasy lithographic ink was applied to a printer's hard rubber roller and then rolled onto the plate until ink adhered to the oleophilic base of the plate. A piece of paper was then placed on the inked plate and a negative copy obtained by pressing the paper and plate together. During the inking operation, the ink adhered to the oleophilic surface of the base while no ink adhered to the hydrophilic areas corresponding to the original unexposed areas. In this manner, several good quality negative, wrong-reading, copies were obtained.

EXAMPLE II

35 Example I was repeated except that Solution A of Example I contained 10 ml. of 0.1 M Na_2S instead of the thiourea and 15 grams of potassium thiocyanate instead of the 20 grams originally added to Solution A. Between development and etching, there was a three minute water wash. The etch-bleach step was the same as in Example I except that a 1% aqueous H_2O_2 solution was used and the bleaching time was 7 minutes. The film was sponged and washed under running water until a clear gelatin relief was obtained in the original unexposed areas while in the exposed area, the image was completely etched to the film base. The film was then mounted on an offset printing press, rubber with a 5% solution of acetic acid and inked in the conventional manner. Many negative right-reading copies having sharp images were obtained.

EXAMPLE III

The photosensitive element of Example I was exposed for 15 sec. in the manner described in Example I. A developer solution was prepared as follows:

Solution C

Water (100° F.)—600 ml.
Sodium sulfite (anhyd.)—100 g.
60 Hydroquinone—30 g.
Ethylene glycol—200 ml.
1-Phenyl-3-pyrazolidone—3 g.
N-Methyl-2-pyrrolidone—3.3 g.
Trisodium salt of ethylenediamine tetraacetic acid—0.5 g.
65 Potassium carbonate (anhyd.)—80 g.
Benzotriazole—1.5 g.
Water to make 1000 ml.

Solution D

70 Water (60° F.)—600 ml.
Ethylene glycol—200 ml.
Trisodium salt of ethylenediamine tetraacetic acid—16 g.
Sodium hydroxide (flakes)—36 g.
75 Water to make 1000 ml.

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Solution E

Solution C—666 ml.
0.1 M Na₂S—20 ml.
Potassium thiocyanate—30 g.
Solution D—666 ml.
Resorcinol—10 g.
Water to make 2000 ml.

The exposed film was silver transfer developed in Solution E for 1 minute and then stopped for 15 seconds in a solution containing 40 ml. of glacial acetic acid and water to make 1 liter.

A bleach-etch solution was then prepared as follows:

Solution F

Solution B (excluding H ₂ O ₂)	-----	ML.
1% H ₂ O ₂	-----	1000
		1000

The silver transfer developed film was bleached in Solution F for 2 minutes and then immersed for 4 minutes in a solution containing 100 ml. of glyoxal and 1900 ml. of water. Bleaching was carried out until the exposed areas were etched to the oleophilic surface of the base and the silver transfer image areas were etched to the hydrophilic gelatin of the emulsion. The film was then mounted on a conventional duplicating machine using phosphoric acid and gum arabic as the fountain solution and standard ink. After a few copies were run, the duplicator was stopped and the plate rubbed with a 1% acetic acid solution. The press was restarted and many negative right-reading copies were obtained. To provide quicker start-up by reducing scum, the plate was also rubbed with a gum arabic-asphaltum solution.

EXAMPLE IV

Example III was repeated except that the developer solution, Solution E, did not contain any sodium sulfide and contained only 8 grams of resorcinol. In this example, the potassium thiocyanate served as the nucleating agent rather than the sodium sulfide. After development for one minute and bleaching as in Example III, the developed element was hardened in a solution of 1 percent mucochloric acid for two minutes. When mounted on the offset press uneven inking occurred for the first 100 copies. The press was stopped and the plate rubbed with the fountain solution of one percent acetic acid. After this treatment and inking, 1000 negative right-reading copies were produced.

EXAMPLE V

Example I was repeated except that a developer solution as follows was used.

Solution G

Solution C—666 ml.
Water—700 ml.
Potassium thiocyanate—30 g.
Resorcinol—8 g.
Potassium bromide—2 g.
Sodium hydroxide—24 g.
Water to make 2000 ml.

After exposure as in Example I, the exposed film was developed for one minute in Solution G and then water-washed for 30 seconds. A bleach-etch solution was prepared as follows:

Solution H

Solution B (excluding H ₂ O ₂)	-----	ML.
3% H ₂ O ₂	-----	500
Water	-----	1000

The film, after development and washing was then bleached in Solution H for 4.5 minutes. The bleached film was not sponged or rubbed but rather, the bleach-etch solution was agitated while the film was immersed in it. There was a good gelatin relief image but a slight film covering remained in the exposed areas due to incomplete etching. Longer etching and bleaching corrected this prob-

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lem. After bleaching, the film was fixed in Solution I for 5 minutes. Solution I was prepared as follows:

Solution I

Water—600 ml.
Na₂S₂O₃ (anhyd.)—153 g.
Na₂SO₃ (anhyd.)—15 g.
KAl(SO₄)₂·12H₂O—20 g.
Na₂B₄O₇·10H₂O—18 g.
Glacial acetic acid—12 ml.
Water to make 2000 ml.

After fixing, the film was water washed for 10 minutes. When tested on the offset press using 1% acetic acid as the fountain solution and printing ink, 1000 negative right-reading copies were obtained. Ink pick-up was improved by rubbing the plate with the fountain solution after copy number 125 and copy number 220.

EXAMPLE VI

Example V was repeated except that developer, Solution G, contained 20 ml. of 0.1 M Ma₂S and did not contain any resorcinol or potassium bromide. The bleach-etch solution was the same as Solution F except that three percent hydrogen peroxide was used in place of one percent peroxide. After development for one minute and water washing for 30 seconds, the film was immersed in a fixer containing 128 grams of Na₂S₂O₃ and 1000 ml. of water for a period of four minutes. The fixing was followed by water washing for two minutes and etching for eight minutes with sponge rubbing of the plate every two minutes during etching. The film was tested on the offset printing press as in Example V. The tests indicated that fixing before etching gives longer plate life when printing and increases the processing latitude in the etching bath. Many good quality negative right-reading copies were obtained.

EXAMPLE VII

The photosensitive element of Example I was exposed for 20 seconds as described in Example I. Developer solutions were prepared as follows:

Solution J

Solution C—666 ml.
Solution D—666 ml.
Water to make 2000 ml.

Solution K

Solution C—666 ml.
Solution D—666 ml.
Potassium thiocyanate—30 g.
Water to make 2000 ml.

The exposed element was conventionally developed in Solution J for one minute and then water washed for 5 seconds. Silver transfer development followed by development in Solution K for one minute and water washing for three minutes. In the unexposed areas, there was a positive mirror-like, surface silver image while in the exposed areas, a black image existed. Transfer development was followed by etching for 2.5 minutes in Solution B as in Example I. Negative copies were then produced as in Example I by the use of a printer's hand rubber roller. Ink adhered to the oleophilic surface of the base while no ink adhered to the gelatin relief image corresponding to the original unexposed areas.

When practicing this invention, etching in the exposed areas must be complete to an oleophilic surface. This surface may be the support. Suitable oleophilic supports include the film formed from the polyesterification product of a dicarboxylic acid and a dihydric alcohol made according to the teachings of Alles, U.S. Pat. 2,779,684, and the patents referred to in the specification of that patent. Other suitable supports are the polyethylene terephthalate/isophthalates of British Pat. No. 766,290 and Canadian Pat. No. 562,672 and those obtainable by condensing terephthalic acid and dimethyl terephthalate with propylene glycol, diethylene glycol, tetramethylene glycol or cyclohexane 1,4-dimethanol (hexahydro-p-xylene alco-

hol). The films of Bauer et al., U.S. Pat. 3,052,543, may also be used. The above polyester films are particularly suitable because of their dimensional stability. Polymerized vinyl compounds; e.g., copolymerized vinyl acetate and vinyl chloride, polystyrene and polymerized acrylate may also be mentioned. Likewise, the cellulosic supports, e.g., cellulose acetate, cellulose triacetate, cellulose mixed esters, etc., may be used. By coating a support with elements having strong oleophilic properties, i.e., Werner-chrome complexes, mercaptans, resins, etc., and then etching only to the coating, it is possible to use many other supports. Other suitable supports may include paper, metals, and alloys or metal oxide coated supports.

The silver halide emulsion may be selected from many well known emulsions containing silver chloride, silver bromide, mixtures thereof, or mixtures thereof containing small amounts of silver iodide.

The preferred hydrophilic organic binder for the silver halide emulsion is gelatin, however, any natural or synthetic water-permeable hydrophilic colloid binder may be used with the proviso that the binder is susceptible to the bleaching and etching of the acid-peroxide bleach solutions.

The emulsions can contain known antifoggants, e.g., 6-nitrobenzimidazole, benzotriazole, triazaindenes, etc., as well as the usual hardeners, i.e., chrome alum, formaldehyde, dimethylol urea, mucochloric acid, etc. Other emulsion adjuvants that may be added comprise suitable pigments, matting agents, plasticizers, toners, optical brightening agents, etc.

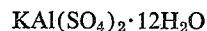
Silver transfer development may be accomplished by using high energy conventional developers which contain silver halide solvents and a silver nucleating agent. The development process may consist of a dual or single bath. The various methods of silver transfer development, suitable developers, and suitable nucleating agents are disclosed in assignee's co-pending applications Blake Ser. No. 401,971, filed Oct. 6, 1964, U.S. Pat. 3,490,905, Jan. 20, 1970, and Strange Ser. No. 494,940, filed Oct. 11, 1965, now abandoned.

The bleach-etch solution are generally of the acid peroxide type and include at least two reactions: (1) oxidation of developed silver and (2) degradation or softening of gelatin. The rates of both reactions depend on halide and metal ion concentrations, hydrogen peroxide concentrations, and pH, the latter generally in the range of 1 to 3.

A satisfactory bleach-etch solution is that disclosed in Example II of British Pat. No. 793,550, published Apr. 16, 1958. The effect of concentration of the various components of the bleach-etch solution are described in Centa, J. M., PSA Journal, 11:22 (1945); Marriage, A., Brit. Journal of Phot., 91:142 (1944); Luckey James, and Vanselow, Phot. Sci. Tech., 2:130 (1955). The bleach-etch solutions contain various concentrations of hydrogen peroxide. Commercially available 30% hydrogen peroxide may be diluted and used if a stabilizer, 0.3 gm. of p-acetophenetide/liter of 3.5% H₂O₂ is added to increase the shelf life of the hydrogen peroxide solutions. Commercially available 3% peroxide does contain suitable stabilizers. After etching, the degraded gelatin is preferably rubbed away to get to the oleophilic surface and the oleophobic relief image. Degradation of the gelatin may also be produced through agitation of the bleach-etch solution while the developed film is being etched. Proper bleaching-etching time is critical and depends upon the concentrations of the etch solutions and the amount of silver transfer development. Where there is sufficient silver transfer development throughout the layer and the film is left in the etching solution for too long a time, the entire emulsion surface may be etched away leaving only the surface of the film support. The average bleach-etch times used for the concentration of the etching solution disclosed herein was usually 1-2 minutes but longer times with lower peroxide concentra-

tion were successfully employed. The process of this invention depends on the difference in etch rate of the gelatin containing chemically developed silver (exposed areas) and the gelatin containing transfer developed silver (unexposed areas), the latter etching at a slower rate than the former due to the concentration of the reduced silver in the surface image.

To increase printing plate life, the developed plate may be treated in conventional fixers, e.g., Na₂S₂O₃ and said fixers may also contain hardeners, e.g.,



Likewise, the etched plate may be immersed in various hardeners, e.g., glyoxal, mucochloric acid, chrome alum, formalin glutaraldehyde, etc.

Rubbing of the printing plate with the fountain solution permits rapid start-up and printing. Suitable fountain solutions include low concentrations of glacial acetic acid, up to 5%; commercially available gum arabic-asphaltum solutions; and gum arabic-phosphoric acid solutions.

Any source of actinic radiation is suitable as the exposure source for this invention. Suitable sources include photographic flood lamps, carbon arcs, electronic flash units, mercury-vapor arcs, etc.

Exposure can be from the front or back of the photosensitive element if a transparent support is used but an element with an opaque support can be exposed from the front.

This process is a simple method of obtaining a negative-working printing plate from the same sheet of film used in the original exposure. The thin hydrophilic relief images produced by this process give sharp images when reproduced on a copy sheet. This process is also useful as a simple method of obtaining copies of information stored on microfilm.

This invention offers the further advantage of producing excellent copies after prolonged use of the plate and has the ability to immediately print satisfactory copies after a period of machine shutdown.

What is claimed is:

1. The process which comprises

- (a) exposing imagewise to actinic radiation an outer light-sensitive colloid silver halide emulsion layer of a photographic film having a flexible film base,
- (b) developing the exposed silver halide areas of said layer,

- (c) developing the unexposed areas of said layer with a silver transfer developer solution either sequentially or simultaneously with step (b), whereby a reduced silver image corresponding to the unexposed areas of the silver halide layer is formed in the top surface of the outer water-permeable organic colloid layer and a reduced silver image corresponding to the exposed areas of the silver halide layer is formed throughout the exposed regions of the silver halide layer,

- (d) bleaching the developed layer resulting from steps (b) and (c) with a gelatin-degrading aqueous acidic peroxide silver bleaching-etching solution, and

- (e) removing the degraded colloid binder and material associated therewith to uncover the oleophilic surface of said film base in the exposed areas and leaving an oleophobic water-permeable colloid-containing surface in the unexposed areas of said layer.

2. A process according to claim 1 wherein said actinic radiation is light in the visible region of the spectrum.

3. A process according to claim 1 wherein said colloid is gelatin.

4. A process according to claim 1 wherein step (c) is carried out in a single aqueous developer solution containing a silver halide solvent and silver nucleating agent.

5. A process according to claim 1 wherein said film base is a polyethylene terephthalate film base.

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6. A process according to claim 1 wherein said silver halide is a mixture of silver bromide and silver chloride.

7. A process according to claim 1 wherein the silver transfer developer solution contains thiourea.

8. A process according to claim 1 wherein the silver transfer developer solution contains potassium thio- 5 cyanate.

9. A process according to claim 1 wherein the silver transfer developer solution contains sodium sulfide.

10. A process according to claim 1 wherein the bleach- 10 ing solution of step (d) contains potassium bromide, cupric nitrate, lactic acid, and hydrogen peroxide.

11. A process according to claim 1 wherein after step (c) the resulting element is treated in a fixing solution containing sodium thiosulfate.

12. A process according to claim 1 wherein after step (e) the resulting element is treated in a hardening solu- 15 tion.

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13. A process according to claim 1 wherein after step (e) the resulting element is used as a lithographic printing plate to transfer inked areas corresponding to the exposed areas to a receptor surface.

References Cited

UNITED STATES PATENTS

2,058,396	10/1936	Baker	96—36.3
2,178,338	10/1939	Frankenburger et al.	96—36.3
2,854,386	9/1958	Lyman et al.	96—36.2
2,856,284	10/1958	Hamm	96—36.3

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