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Maffet et al.

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[54] **TREATING A DEVELOPED GELATIN SILVER HALIDE EMULSION LAYER ELEMENT WITH ACETIC ACID AND DISCHROMATE IONS**

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Related U.S. Application Data

[63] Continuation of Ser. No. 666,277, Sept. 8, 1967, abandoned.

[52] **U.S. Cl.** **101/450,** 96/33, 101/466, 101/456

[51] **Int. Cl.** **G03f 7/02,** B41m 1/00

[58] **Field of Search** 96/33, 60; 101/450

[56] **References Cited**

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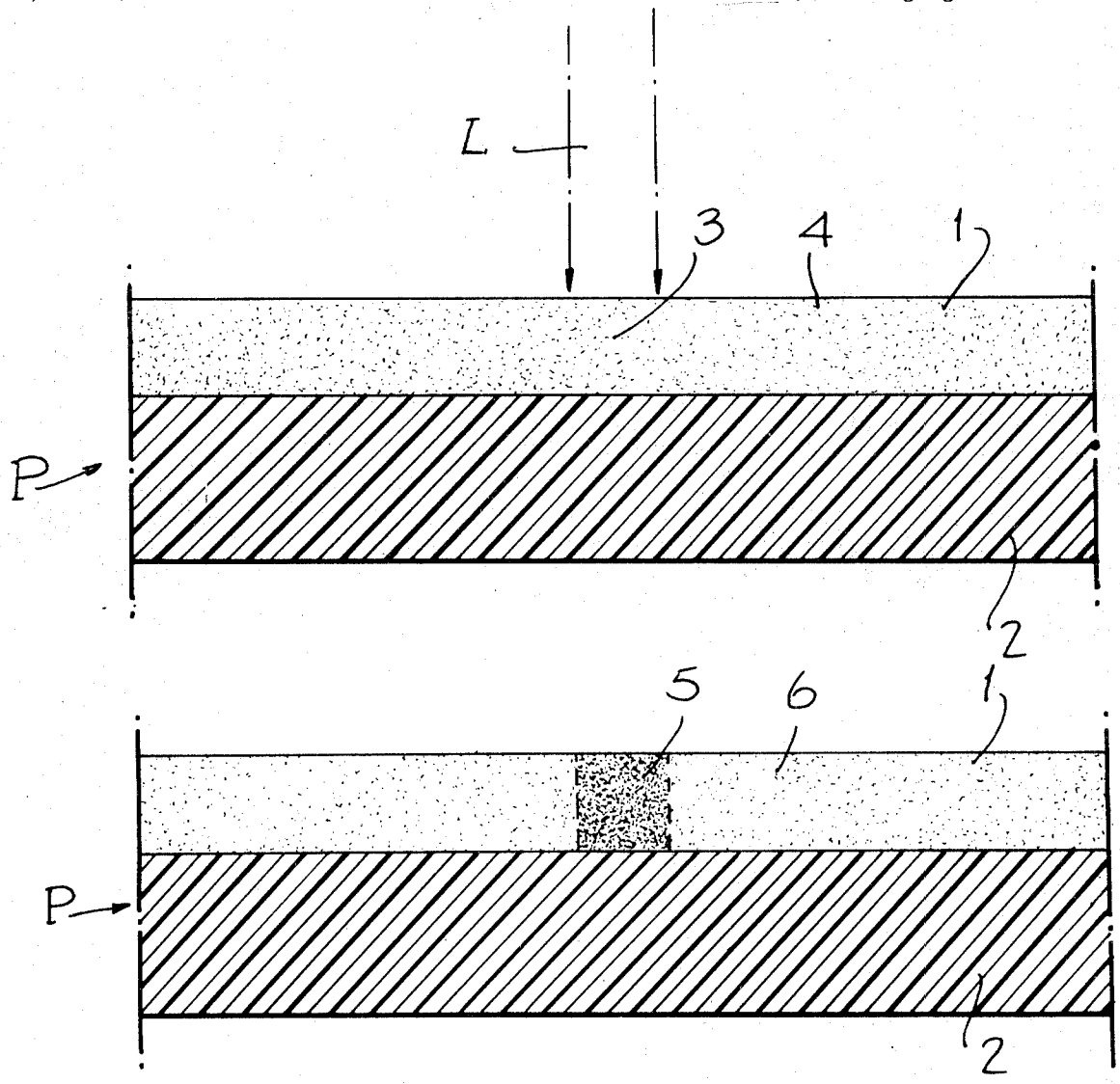
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[57] **ABSTRACT**

This invention relates to the production of a positive-printing lithographic printing plate. The process utilizes an improved stop-bath solution which may be used with a wide variety of emulsions and developer solutions. One of the outstanding features of the invention is that exposure of the plate element to a positive original results in development of the plate element as a photographic negative image which will enable a press to print a positive copy. This is accomplished by treating the photographically developed plate in a stop-bath containing an oxidizing agent, such as potassium dichromate, which is capable of reacting with unoxidized developing agent, such as hydroquinone, in the non-image areas of the plate to make these areas oleophilic through a mechanism akin to polymerization or tanning.

4 Claims, 2 Drawing Figures



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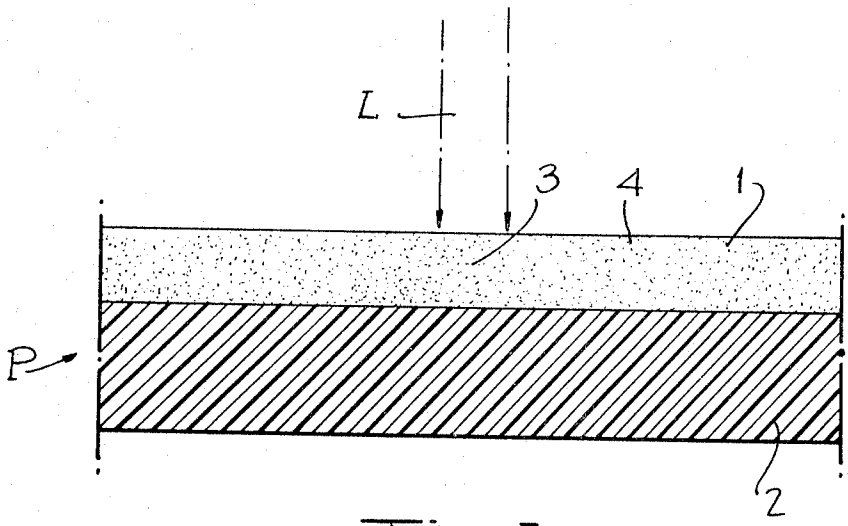


Fig. 1.

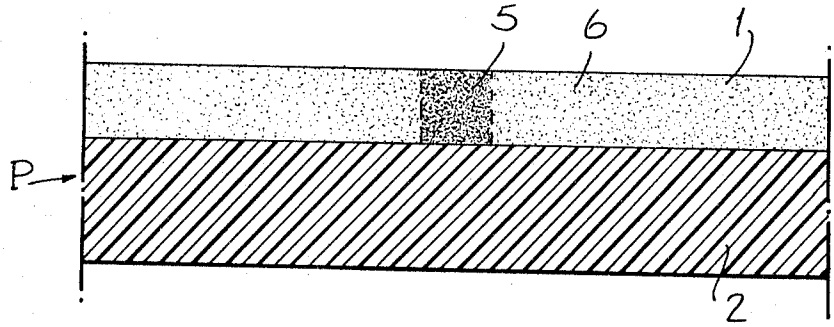


Fig. 2.

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TREATING A DEVELOPED GELATIN SILVER HALIDE EMULSION LAYER ELEMENT WITH ACETIC ACID AND DISCHROMATE IONS

This application is a continuation of Ser. No. 666,277 filed Sept. 8, 1967, now abandoned.

BACKGROUND OF THE INVENTION

This invention relates to lithography and particularly, to the production of a positive-printing lithographic printing plate. More particularly, the invention relates to a lithographic plate made by a photographic process wherein the plate element develops as a photographic negative image and prints a positive copy.

The positive-printing plate to which the invention is directed is of the type known in the trade as lithographic, i.e., the plate surface is planar. In this type of plate, printing does not depend upon adjacent surfaces being raised or depressed relative to each other as in gravure and intaglio plates, but is dependent upon the differential oleophobic/oleophilic character of adjacent coplanar surfaces.

Conventional processes for the production of lithographic plates involve making a plate element by applying a photographic emulsion to a base support, exposing the plate element to light rays from an object, and developing the exposed plate element to form an oleophilic image. In general, the photographic emulsion comprises a light sensitive agent, such as a silver halide, in a hydrophilic binder, such as gelatin. Exposure of such an emulsion to light, and subsequent treatment in an alkaline solution in the presence of a developing agent, such as hydroquinone, results in reduction of the exposed silver halide to metallic silver and, generally, a corresponding hardening of the gelatin and formation of an oleophilic image. Oxidation of a developing agent reduces a silver compound in the emulsion and forms an oleophilic image. Thus, the conventional processes result in plates wherein the exposed areas are ink receptive and the unexposed areas are non-ink receptive. Illustrative of such processes is that described in U. S. Pat. Re. No. 25,885.

The production of photographic printing plates wherein the unexposed areas are ink receptive is also known. However, such processes involve removal of unhardened portions of the photographic emulsion resulting in a non-planar surface. Hence, these processes cannot be employed to produce lithographic printing plates. Illustrative thereof are the processes disclosed in U. S. Pat. Nos. 1,042,827; 1,482,612; 1,482,615; 1,482,616 and 1,484,029 and British Pat. Nos. 262,531 and 518,662. Of similar import are the processes described in British Pat. Nos. 210,862 and 729,409 wherein printing plates are produced with emulsions comprising light sensitive, oleophilic diazo compounds. Exposure to light modifies the diazo compounds to render them non-oleophilic. While the non-exposed areas are, thus, ink receptive, the printing plate produced is not planographic since the modified (exposed) diazo is removed to produce a relief image.

Accordingly, a principal object of the present invention is to provide a method of making a positive printing lithographic printing plate.

Another object of the invention is to provide a method of making a lithographic printing plate by a photographic process wherein the plate element develops as a photographic negative and prints a positive copy.

Still another object of the invention is to provide a positive printing lithographic printing plate.

Other and further objects of the invention will be obvious upon an understanding of the illustrative embodiment about to be described, or will be indicated in the appended claims, and various advantages not referred to herein will occur to one skilled in the art upon employment of the invention in practice.

A preferred embodiment of the invention has been chosen for purposes of illustration and description and is shown in the accompanying drawings, forming a part of the specification wherein:

FIG. 1 is a diagrammatic view showing a photosensitive plate during exposure; and

FIG. 2 is a similar view showing the plate after development.

SUMMARY OF THE INVENTION

The invention relates to a positive-printing lithographic printing plate and the method for its production.

In general in practicing the method of this invention, a photographic emulsion 1 is applied to a substrate or base support 2 to produce a plate element P. This plate element is exposed to light rays L from a subject, e.g., a positive original or a film negative to form an exposed area 3 and an unexposed area 4.

The exposed plate element is then treated with a developer solution to produce a developed photographic negative image 5 of the subject. The image 5 may be either a photographic negative image if the object is a positive or a photographic positive image (i.e., a reverse negative image) if the object is a negative.

Treatment of the developed plate element with a stop-bath solution imparts oleophilic properties to unexposed areas 4 and oleophobic properties to the exposed areas 3 so that the areas 5 are oleophobic and the non-image areas 6 are oleophilic. The resultant plate is thus provided with oil receptive and non-oil receptive areas corresponding to unexposed and exposed areas, respectively. Accordingly, on a press the printing plate of this invention will produce a positive reproduction of the subject to which it has been exposed.

The invention contemplates the production of positive-printing lithographic printing plates utilizing essentially conventional photographic emulsions and developer solutions, but employing a modified stop-bath solution.

Photographic emulsions conventionally comprise a light sensitive agent in admixture with a binder. Suitable light sensitive agents for the practice of the invention comprise the silver halides, including silver iodobromochloride, silver iodobromide and silver bromochloride. Suitable binders comprise the hydrophilic binders such as gelatin.

Developer solutions may be employed in wide variety and include those ordinarly used with litho films, X-ray films, conventional negative films positive print films and papers, etc.

The stop-bath solution utilized in the present invention comprises a solution containing an oxidizing agent effective in forming an oleophilic reaction product in the unexposed areas of the emulsion after development. The latter may be any oxidizing agent effective in forming an oleophilic reaction product in the unexposed areas of the emulsion after development. Optimum results appear to be achieved with a dichormate

oxidizing agent and accordingly, such oxidizing agent is preferred, although the invention may be practiced with other oxidizing agents, e.g., hydrogen peroxide. Acidification of the stop-bath is desirable for the purpose of lowering the pH and halting the development process. Acetic acid has been found to be suitable for this purpose.

In the practice of the invention a photographic emulsion **1**, e.g., a mixture of silver iodobromochloride in gelatin is prepared and coated onto a base support **2**. The latter may be any suitable support material and is not critical since the differential ink receptivity of the plate surface is the determining and controlling factor anent printing ability. Exposure to actinic radiation induces the formation of latent images in the exposed silver halide and, on subsequent treatment with a developing agent, reduction of all or part of the silver halide to metallic silver in the exposed areas.

The developer solution includes a reducing agent, such as hydroquinone, which reduces the silver halide in the exposed area to produce an image characterized by a differential density proportional to the intensity of the light incident on the plate during exposure. Accordingly, the image produced on the plate will be a negative with respect to the subject. Following development, there are differential quantities of oxidized and non-oxidized developing agent corresponding to respectively, the exposed and unexposed areas.

Treatment of the developed plate with an acidic stop-bath solution containing an oxidizing agent such as, for example, potassium dichromate, in an aqueous solution acidified with acetic acid, forms an oleophilic reaction product in the unexposed areas, i.e., the non-image areas. It is believed that a reaction between the oxidizing agent and the unreacted developing agent results in the formation of an oleophilic gelatin complex akin to a polymer. Since there is virtually no unreacted hydroquinone in the exposed areas, no polymer is formed and exposed areas remain ink repellant.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the course of the investigation leading to the present invention a number of lithographic printing plates were prepared by coating a photographic emulsion onto a base support, exposing the supported emulsion or plate element to light from a subject, treating the exposed plate element with a developer solution for 30 seconds and treating the developed plate element with a stop-bath solution for 30 seconds. The resulting plates were then placed in a lithographic printing press and inked. In all plates the ink receptive regions corresponded to the unexposed, i.e., non-image areas. The details of preparation and the results of tests on a printing press are presented in tabular form.

Table I lists the compositions and coating weights of the various photographic emulsions employed.

TABLE I

Emulsion	Silver halide	gelatin weight ratio Ag	g HCHO per 1000 gelatin	coating wt in mg/ft²	Reducing agent (per mol silver halide)
E1	silver iodobromo-chloride	1.5/1	19.8	550	—
E2	silver bromo-chloride	3/1	27	550	—
3	silver iodobromo-chloride	1.75/1	14	200	—
E1H	silver iodobromo-chloride	1.5/1	19.8	550	33.3 gms hydro-quinone
E1C	silver iodobromo-chloride	1.5/1	19.8	550	53 g chloro-hydroquinone
E1HM	silver iodobromo-chloride	1.5/1	19.8	550	33.3 hydro-quinone plug 8.3 g p-methylamin-ophenol sulfate
E4	silver iodo-bromide	1.5/1	19.8	550	—

Tables II and III show the compositions of the various solutions utilized in the developer and stop-bath, respectively. In each of these tables the compositions are given for a liter of aqueous solution.

TABLE II

Developer	Composition	
D1	p-methylaminophenol sulfate	1.25 g
	sodium sulfite (anhydrous)	20.0 g
	hydroquinone	5.4 g
	sodium carbonate (monohydrate)	28.5 g
	potassium bromide	0.8 g
	sodium tetraphosphate	0.8 g
	pH = 10.25	
D2	sodium carbonate (monohydrate)	58.0 g
	sodium hydroxide	12.0 g
	sodium thiosulfate	10.0 g
	hydroquinone	6.0 g
D3	commercial litho developer of A-B type	
D4	commercial preparation for developing medical x-ray films	
D5	hydroxylamine hydrochloride	20 g
	pH = 11.5 (by addition of sodium hydroxide)	
D1 S	D1 plus an additional 20 g of sodium sulfite	
D1SA	D1S plus sufficient sodium hydroxide to raise pH to 11.5	
D1-M	D1 without p-methylaminophenol sulfate	
D1C-HM	D1 without hydroquinone and p-methylaminophenol sulfate but with an additional 7.8 g chlorohydroquinone	
D1Z-HM	D1 without hydroquinone and p-methylaminophenol sulfate but with an addition of 7.8 g 1-phenyl-3-pyrazolidone	
D1SB-P	D1S without sodium tetraphosphate but with an addition of 5 g sodium metaborate	
D2-H	D2 without hydroquinone	
D2C-H	D2-H with an addition of 7.8 g chlorohydroquinone	
D2M-H	D2-H with an addition of 18.6 g p-methylaminophenol sulfate	

TABLE III

Stop-Bath	Composition	
S1	potassium dichromate	12.5 g
	glacial acetic acid	20.0 ml
	Water to make 1000 ml	
S2	$Cr_2O_3 \cdot 9H_2O$	17.0 g
	glacial acetic acid	20.0 ml
	Water to make 1000 ml	

Table IV sets forth the combinations of photographic emulsion, developer and stop-bath employed in the various lithographic printing plates prepared and remarks on press performance. With the exception of Plate No. 15, all plates were exposed to light from a positive original.

TABLE IV

Plate No.	Emulsion	Developer	Stop-Bath	Observations on Press Performance*
1	E1	D1	S1	

2	E2	D1	S1	
3	E1	D1S	S1	Distinct improvement over Plate Nos. 1 & 2 as to "scumming"
4	E2	D1S	S1	Distinct improvement over Plate Nos. 1 & 2 as to "scumming"
5	E3	D1S	S1	Some tendency to "scumming"
6	E1	D2	S1	
7	E1	D2	S1	
8	E1	D2C-H	S1	
9	E1	D2M-H	S1	
10	E1	D1-M	S1	
11	E1	D1C-HM	S1	
12	E1	D1Z-HM	S1	
13	E1	D3	S1	
14	E1	D4	S1	
15**	E1	D1S	S1	Outstanding reproduction with fine detail
16	E1	D5	S1	
17	E1	DiSB-P	S1	Still further improvement in quality over Plate No. 3 as to print density and "scumming"
18	E1H	D2-H	S1	
19	E1C	D2-H	S1	
20	E1HM	D2-H	S1	
21	E1	D2S	S2	Light density
22	E4	D1S	S1	

* In all cases a positive copy of subject was obtained on the press.
** Exposed to light from a microfilm negative.

It will be appreciated from an examination of the foregoing tabulated data that the invention is operable with a wide variety of photographic emulsions and is readily workable in a vast array of developer solutions with many different developing agents. The data amply demonstrate that the general system requirements for production of a positive-printing lithographic printing plate are an emulsion of a light-sensitive agent, a photographic developer and a stop-bath containing an oxidizing agent capable of forming an oleophilic reaction product when contacted with non-oxidized developer in the presence of the emulsion.

As various changes may be made in the form, construction and arrangement of the parts herein without departing from the spirit and scope of the invention and without sacrificing any of its advantages, it is to be understood that all matter herein is to be interpreted as illustrative and not in a limiting sense.

We claim:

1. The method of making a planographic printing plate which method comprises:

exposing to light modulated by an original plate element support having a light sensitive gelatinous silver halide emulsion layer thereon,

developing the exposed silver halide emulsion layer with a silver halide developing agent selected from the group consisting of hydroquinone, hydroxylamine hydrochloride, 1-phenyl-3-pyrazolidone or p-methylamino phenol sulphate, capable of forming in a reaction with an oxidizing agent selected from the group consisting of dichromate ions and hydrogen peroxide, a reaction product capable of rendering photographic gelatin receptive to lipophilic ink,

subsequently treating the developed silver halide emulsion layer which contains residual unoxidized developing agent in the non-silver image portions with an aqueous acidic solution containing acetic acid and said oxidizing agent thereby making said non-silver image portions selectively receptive for lipophilic ink.

2. The method of making a planographic printing plate which method comprises:

exposing to light modulated by an original plate element support having a light sensitive gelatinous silver halide emulsion layer thereon,

developing the exposed silver halide emulsion layer with a hydroquinone developing agent forming a silver image under alkaline developing conditions,

subsequently treating the developed silver halide emulsion layer with an acidic aqueous solution containing acetic acid and dichromate ions that react with the unoxidized hydroquinone left in the non-silver image portions thereby making said portions selectively receptive for a lipophilic ink used in lithographic printing.

3. The method as claimed in claim **2,** wherein the dichromate ions are yielded by potassium dichromate.

4. A method for making planographic prints which method comprises:

exposing to light modulated by an original plate element support having a light sensitive gelatinous silver halide emulsion layer thereon,

developing the exposed silver halide emulsion layer with a hydroquinone developing agent forming a silver image under alkaline developing conditions,

subsequently treating the developed silver halide emulsion layer with an acidic aqueous solution containing acetic acid and dichromate ions that react with the unoxidized hydroquinone left in the non-silver image portions thereby making said portions selectively receptive for a lipophilic ink used in lithographic printing,

contacting the thus treated silver halide emulsion layer with a lipophilic planographic printing ink that becomes selectively recepted by the non-silver image portions and

transferring that recepted ink from said silver halide emulsion layer by contacting with printing stock material used in planographic printing.

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