June 20, 1967 T. I. ABBOTT ETAL 3,326,685

LITHOGRAPHIC PROCESS USING A STOP BATH

Filed April 27, 1964

FIG. 1

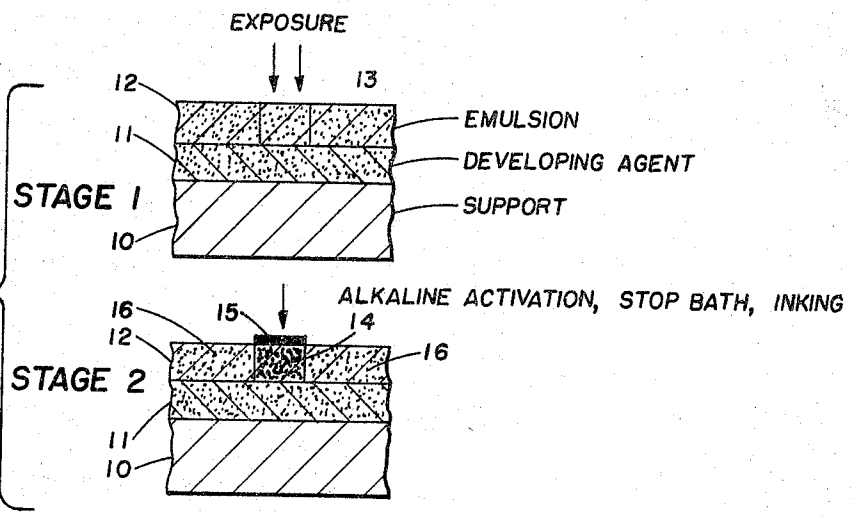
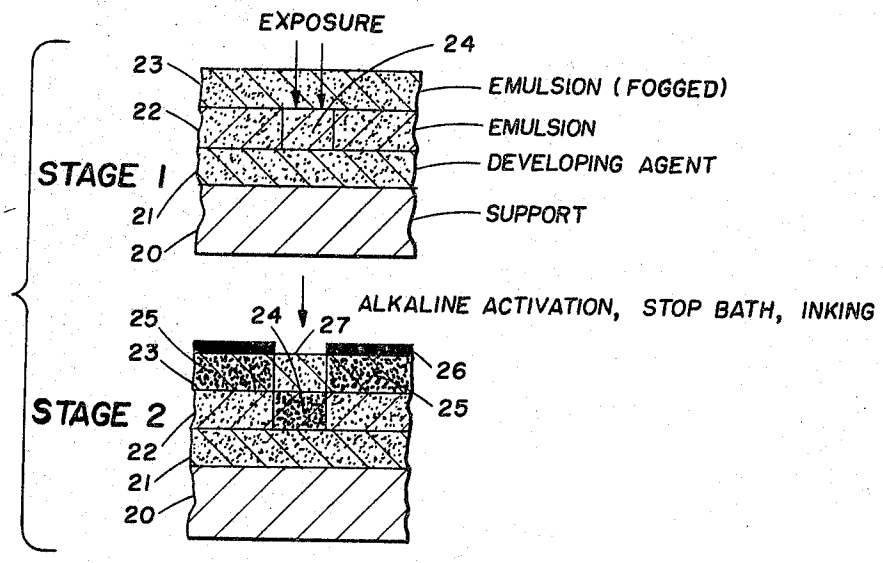


FIG. 2



THOMAS I. ABBOTT
EDWARD C. YACKEL
INVENTORS

BY R. Frank Smith
Henry C. Byers
ATTORNEYS

United States Patent Office 3,326,685 Patented June 20, 1967

3,326,685

LITHOGRAPHIC PROCESS USING A STOP BATH

Thomas I. Abbott and Edward C. Yackel, Rochester, N.Y., assignors to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey

Filed Apr. 27, 1964, Ser. No. 362,699
20 Claims. (Cl. 96—62)

This invention concerns photographic lithographic printing plates comprising a silver halide photographic emulsion and, more particularly, a stop bath for use in processing these lithographic printing plates.

In our U.S. patent application Ser. No. 861,125, filed Dec. 21, 1958, now Patent No. 3,146,104, we disclose a photographic method for preparing lithographic printing plates involving the formation of a developable silver halide image in a hydrophilic organic colloid-silver halide film.

The exposed plates are normally developed in an alkaline activator and then placed in an acid stop bath before being placed on the printing press or offset duplicator. In our invention, we have found that the addition of norbornylene glycol to the acid stop bath improves the lithographic differentiation of the plate by making the background more water-receptive without affecting the ink receptivity of the image. This makes the plate less susceptible to scumming or background inking when it is used on the printing press.

One object of this invention is to provide a process for obtaining a photographic lithographic printing plate having improved resistance to scumming. Another object is to provide an improved acid stop bath for processing lithographic printing plates. An additional object is to provide a process for improving the lithographic differentiation of the plate by making the background more water-receptive without affecting the ink- receptivity of the image. Additional objects will be apparent from the following disclosure.

The above objects are obtained by using a stop bath containing norbornylene glycol along with a solvent for the norbornylene glycol and an acid such as phosphoric acid.

The following concentrated stop bath formula gives our preferred composition:

	Percent by weight
Norbornylene glycol	24.0
Phosphoric acid (85%)	13.2

This formulation is a concentrated form which is diluted with water to make a working solution as required for the particular photographic plate to be processed. Dilution of this concentrate to about 1:8 with water is recommended as a good working solution.

The norbornylene glycol is the critical component of the stop bath and can be varied between about 1 to 15% by weight of the working stop bath solution depending upon the printing conditions.

Preferably water is a useful solvent. However, other common solvents can be used. For instance, other common solvents which can be used include ethyl alcohol, 2-ethoxy-ethanol, and the like. It will be appreciated that since there is a large number of common solvents, a listing of every common solvent here would not be practical.

Although phosphoric acid is the preferred acid, it will be appreciated that other acids can be used which have a dissociation constant from about 1×10^{-2} to 1×10^{-5}, such aas acetic acid, glycolic acid, citric acid, etc. The amount of acid may be from 1 to 10% by weight of the working solution, so that the solution has a pH of about 2–4.5.

In the accompanying drawings, representative sensitive elements of the process are shown in greatly enlarged

cross-sectional views at various stages of the preparation of lithographic printing plates.

In FIG. 1 a negative-positive process is illustrated and in FIG. 2 is shown a positive-positive process.

In FIG. 1, layer **10** of the element of Stage **1** represents a support such as paper, film base, etc., layer **11** is a hydrophilic agent and a quantity of black colloidal silver or carbon black, etc., for antihalation protection, layer **12** a gelatino-silver halide emulsion layer for recording the line or halftone image.

In the process of FIG. 1, after exposure to a subject as shown in area **13**, followed by alkaline activation, stop bath, and inking, the element appears substantially as shown in Stage **2**, area **14** being composed of silver and the reaction product of the oxidized developing agent and the hydrophilic organic colloid present in the silver halide emulsion layer produced in the development reaction, carrying the ink image **15**, the undeveloped area **16** of layer **12** remaining hydrophilic and repellent of printing ink when moistened with water.

In FIG. 2 is shown a positive-positive system in Stage **1** of which the element includes a support **20** such as a paper or film support, layer **21** an antihalation hydrophilic colloid layer containing developing agent and black colloidal silver, carbon black, etc., layer **22** a hydrophilic organic colloid silver halide emulsion layer, and layer **23** a fogged silver halide emulsion layer. Upon image exposure in region **24** followed by alkaline activation, stop bath and inking, the element appears substantially as shown in Stage **2**, the silver halide developing agent of layer **21** which has not been utilized in developing the negative silver image in area **24** of layer **22** having developed a positive silver halide image to silver in areas **25** of layer **23**. The ink images **26** are accepted in areas **25** which are composed of silver and the reaction product of the hydrophilic organic colloid present in the silver halide emulsion layer and the oxidized developing agent. The remaining areas **27** are hydrophilic and repel printing ink when the plate is moistened in the lithographic printing press.

In the sensitive elements described, the emulsion layers should be substantially hardened, particularly the outermost emulsion layer, e.g. layer **12** of FIG. 1 and layer **23** of FIG. 2, in order to prevent the alkaline activated, stopped and inked emulsions from adhering to printing blankets, printing paper, etc. For this purpose, the emulsion should be as hard as a gelatin layer containing at least about 2 grams and preferably from about 2 to 15 grams of dry formaldehyde per pound of gelatine.

In the preferred arrangement, the developing agent is incorporated in a separate layer under the silver halide emulsion layer since this arrangement gives improved sharpness, latitude and better quality ink images than when the developing agent is incorporated directly in the emulsion layer.

The following examples are intended to illustrate our invention but not to limit it in any way.

Example 1

The element of FIGURE 1 was exposed to a line negative, then activated for 20 seconds in a 4 percent solution of sodium carbonate monohydrate.

The film was placed in a 2 percent phosphoric acid stop bath for 20 seconds and then placed on a Model 1250 Multilith Duplicator using VanSon ink and Repelex fountain solution.

The resulting printed copy had considerable scum in the background areas.

A duplicate photographic printing plate prepared employing the stop bath disclosed above in our preferred embodiment, diluted to contain about 2% phosphoric acid for 20 seconds and run on the same duplicator with the same ink and fountain solution gave printed copy which

had a crisp black image and no traces of background scumming.

Example 2

The element of FIGURE 1 was exposed and processed as described in Example 1.

A 2% phosphoric acid stop bath was used and considerable trouble with scum was encountered on the printed copies using Addressograph Multigraph ink, ML–36 and the Repelex fountain solution. A stop bath having our preferred formulation diluted to contain about 2% phosphoric acid was substituted for the phosphoric acid stop bath and the printed copy from the photographic plate treated in this manner showed no scum problem. This process with the same formulation of the improved stop bath was used for a period of five weeks without encountering any scumming problem.

Example 3

The sensitive element of FIGURE 2 was exposed to a line positive, processed 60 seconds in 4% aqueous sodium carbonate monohydrate solution, treated in a 2% aqueous acetic acid stop bath for 1 minute and squeegeed to remove excess liquid.

This plate was used on an A. B. Dick Duplicator using A. B. Dick 21010 ink and Repelex fountain solution. Considerable scum was encountered in the resulting prints. A duplicate print was then prepared and processed as above employing our preferred embodiment diluted to contain about 2% phosphoric acid as the stop bath. No scum was encountered.

The Repelex fountain solution used in this invention is disclosed in Van Dusen U.S. Patent 2,393,875, issued Jan. 29, 1946.

Example 4

The element of FIGURE 1 was exposed to a line negative then activated for 20 seconds in a 4% solution of sodium carbonate monohydrate.

The film was placed in a 2% phosphoric acid stop bath which also contained 5% triethylene glycol for 1 minute and squeegeed to remove excess liquid.

The plate was used as in Example 1. Considerable scum was encountered in the resulting prints.

Many treatments are known to improve ink-water differentiation and prevent scumming on lithographic plates. Pretreatment of the plate with an acid solution of acetamide has been used to increase the hydrophilicity of the plate. Scumming of inks, particularly those with slow drying characteristics, can often be prevented by the addition of ethylene glycols or polyglycols such as Carbowax 600 to the inks used for lithographic printing. Fountain solutions are sometimes modified with formamide to prevent scumming. When the stop bath of our invention is used, such modification of the ink or solutions is not necessary.

The norbornylene glycol may be prepared according to the process of U.S. Patent 2,968,646. A mixture of isomers, or a single isomer by itself, may be used in this invention.

In the concentrated solution we can have from 16–40% by weight of norbornylene glycol and from 8–13% of acid. In our preferred embodiment, the concentrated solution is buffered with sodium dihydrogen phosphate. However, buffering is not necessary nor is the particular buffering agent critical.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. A concentrated photographic stop bath for use with lithographic printing plates comprising about 16–40% by weight norbornylene glycol and about 8–13% by weight of an acid having a dissociation constant of about 1×10^{-2} to 1×10^{-5}.

2. A concentrated photographic stop bath for use with lithographic printing plates comprising about 16–40% py weight norbornylene glycol and about 8–13% by weight acid selected from the class consisting of phosphoric acid, acetic acid, glycolic acid and citric acid.

3. A concentrated photographic stop bath for use with lithographic printing plates comprising about 16–40% by weight norbornlyene glycol and about 8–13% by weight phosphoric acid.

4. A concentrated photographic stop bath for use with lithographic printing plates comprising about 16–40% by weight norbornylene glycol and about 8–13% by weight acetic acid.

5. A concentrated photographic stop bath for use with lithographic printing places comprising about 16–40% by weight norbornylene glycol and about 8–13% by weight glycolic acid.

6. A concentrated photographic stop bath for use with lithographic printing plates comprising about 16–40% by weight norbornylene glycol and about 8–13% by weight critic acid.

7. A concentrated photographic stop bath for use with lithographic printing plates comprising about 16–40% by weight norbornylene glycol and about 8–13% by weight sodium dihydrogen phosphate.

8. A photographic stop bath for use with lithographic printing plates comprising an aqueous solution and between about 1–15% by weight norbornylene glycol and about 1–10% by weight of an acid having a dissociation constant of about 1×10^{-2} to 1×10^{-5}.

9. A photographic stop bath for use with lithographic printing plates comprising an aqueous solution and between about 1–15% by weight norbornylene glycol and about 1–10% by weight of an acid selected from the class consisting of phosphoric acid, acetic acid, glycolic acid and citric acid.

10. A photographic stop bath for use with lithographic printing plates comprising an aqueous solution and between about 1–15% by weight norbornylene glycol and about 1–10% by weight of phosphoric acid.

11. A photographic stop bath for use with lithographic printing plates comprising an aqueous solution and between about 1–15% by weight norbornylene glycol and about 1–10% by weight of acetic acid.

12. A photographic stop bath for use with lithographic printing plates comprising an aqueous solution and between about 1–15% by weight norbornylene glycol and about 1–10% by weight of glycolic acid.

13. A photographic stop bath for use with lithographiic printing plates comprising an aqueous solution and between about 1–15% by weight norbornylene glycol and about 1–10% by weight of citirc acid.

14. A photographic stop bath for use with lithographic printing plates comprising an aqueous solution and between about 1–15% by weight norbornylene glycol and about 1–10% by weight of sodium dihydrogen phosphate.

15. The process of producing a lithographic printing plate from an exposed photographic element comprising a support having thereon a gelatin layer containing therein a silver halide developing agent capable of oxidation in the presence of a hydrophilic organic colloid to form an image receptive to greasey printing ink, and over said gelatin layer an exposed hydrophilic organic colloid silver halide emulsion uniformly hardened with a hardener, such that the colloid has a hardness equivalent to that of a gelatin layer containing from about 2 grams to about 15 grams of dry formaldehyde per pound of gelatin, comprising:

(a) initiating the development of the exposed emulsion layer with an alkaline solution, thereby forming an image, and

(b) arresting the developing action by means of an aqueous solution containing 1–15% by weight nor-

bornylene glycol and about 1–10% by weight of an acid having a dissociation constant of about 1×10^{-2} to 1×10^{-5}.

16. The process of producing a lithographic printing plate from an exposed photographic element comprising a support having thereon a gelatin layer containing therein a silver halide developing agent capable of oxidation in the presence of a hydrophilic organic colloid to form an image receptive to greasy printing ink, and over said gelatin layer an exposed hydrophilic organic colloid silver halide emulsion uniformly hardened with a hardener, such that the colloid has a hardness equivalent to that of a gelatin layer containing from about 2 grams to about 15 grams of dry formaldehyde per pound of gelatin, comprising:

(a) initiating the development of the exposed emulsion layer with an alkaline solution, thereby forming an image, and

(b) arresting the developing action by means of an aqueous solution containing 1–15% by weight norbornylene glycol and about 1–10% by weight of an acid selected from the class consisting of phosphoric acid, acetic acid, glycolic acid and citric acid.

17. The process of claim **16** in which the acid is phosphoric acid.

18. The process of claim **15** in which the aqueous solution contains sodium dihydrogen phosphate.

19. The process for producing a silver image in an exposed photographic element comprising a support having thereon in order, a first layer comprising a silver halide developing agent capable of oxidation in the presence of a hydrophilic organic colloid to form an image receptive to greasy printing inks, a second layer comprising an exposed hydrophilic organic colloid silver halide emulsion and the third layer comprising a fogged hydrophilic organic colloid silver halide emulsion uniformly hardened with a hardener, such that the colloid has a hardness equivalent to that of a gelatin layer containing from about 2 grams to about 15 grams of dry formaldehyde per pound of gelatin, comprising:

(a) initiating the development of the exposed sensitive element with an alkaline solution thereby forming a negative image in the second layer and a positive image in the third layer resulting from the migration to the third layer of the unused silver halide developing agent present in the unexposed areas of the second layer, and

(b) arresting the developing action by means of an aqueous solution containing 1–15% by weight norbornylene glycol and about 1–10% by weight of an acid having a dissociation constant of about 1×10^{-2} to 1×10^{-5}.

20. The process for producing a silver image in an exposed photographic element comprising a support having thereon in order, a first layer comprising a silver halide developing agent capable of oxidation in the presence of a hydrophilic organic colloid to form an image receptive to greasy printing inks, a second layer comprising an exposed hydrophilic organic colloid silver halide emulsion and the third layer comprising a fogged hydrophilic organic colloid silver halide emulsion uniformly hardened with a hardener, such that the colloid has a hardness equivalent to that of a gelatin layer containing from about 2 grams to about 15 grams of dry formaldehyde per pound of gelatin, comprising:

(a) initiating the development of the exposed sensitive element with an alkaline solution thereby forming a negative image in the second layer and a positive image in the third layer resulting from the migration to the third layer of the unused silver halide developing agent present in the unexposed areas of the second layer, and

(b) arresting the developing action by means of an aqueous solution containing 1–15% by weight norbornylene glycol and about 1–10% by weight of an acid selected from the class consisting of phosphoric acid, acetic acid, glycolic acid and citric acid.

References Cited

UNITED STATES PATENTS

3,146,104	8/1964	Yackel et al.	96—33
3,146,105	8/1964	Wrisley et al.	96—33

NORMAN G. TORCHIN, *Primary Examiner.*

J. CANNON, *Assistant Examiner.*