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2,988,988

METHOD OF ETCHING AND DAMPENING PLANOGRAPHIC PRINTING PLATES AND FOUNTAIN SOLUTION THEREFOR

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This invention relates to an etching and dampening or so-called fountain solution for use upon planographic printing plates.

Lithographic printing, which is a type of planographic printing, is a well-known and established art. In general, the process involves printing from a flat (hence the term "planographic") plate depending upon different properties of the image and non-image areas for printability. In lithography the non-image areas are hydrophilic while the image areas are hydrophobic. In the lithographic printing process, a fountain solution is applied to the plate surface which wets all portions of the surface not covered by the hydrophobic image. This solution keeps the plate moist and prevents it from scumming up when the machine is stopped temporarily. An ink roll coated with a grease-based printing ink contacts the image surface depositing the lithographic ink only on the image areas—the hydrophilic non-image areas repelling the ink. The ink image may then be transferred directly to a paper sheet or other receptive surface but generally is transferred to a rubber offset blanket which in turn transfers the print to a final paper sheet. Hence, for each print made during a run, the planographic plate is first dampened with the aqueous fountain solution and then inked with a lithographic ink and finally printed.

The quality obtainable from planographic printing is quite high, approaching that of letter press printing. In addition, planographic plates may be used to obtain runs as long as one hundred thousand prints. However, the methods of placing images on planographic plates is generally a cumbersome and expensive procedure.

A planographic plate comprises either a zinc or aluminum sheet especially treated to make it water-receptive or, for shorter plate runs, comprises a paper base having high wet strength coated with a hydrophilic coating comprising a finely-divided pigment dispersed in a hydrophilic adhesive such as casein. Methods of placing images on such plates comprises typing using a special ribbon, writing on the plate with a grease pencil or utilizing a special photographically sensitized master whereby the image may be formed photographically.

More recently, a novel method known as xerography has come to the fore as a means of applying an image to a lithographic printing plate. The general xerographic process is described in U.S. 2,297,691 to Chester F. Carlson. As there described, the process, in general, comprises placing an electrostatic charge on a xerographic plate, exposing the plate to an image of light and shadow to be reproduced whereby the electrostatic charge is removed in those areas of the plate receiving light, thus producing an electrostatic charge pattern on the plate surface exactly corresponding to the original to be reproduced, contacting the plate bearing the electrostatic latent image with a finely-divided electroscopic marking material whereby the electrostatically charged marking particles deposit on the plate in image configuration. The powder image may then be transferred to any desirable image support base such as paper or, in the application described herein, to a lithographic plate.

The most generally used method of development in xerography is the cascade development method as described in U.S. 2,618,552 to E. N. Wise. However, other methods of development may be used such as powder

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cloud development, as described in U.S. 2,725,304 to Landrigan et al., or magnetic brush development wherein the finely-divided powder particles, called toner, are carried by iron filings (due to electrostatic attraction) which in turn are attracted magnetically by a permanent magnet. By merely brushing the surface of the plate with the clump of filings clinging to the end of the magnet, toner is removed by the electrostatic image which is thus developed or made visible.

The xerographic plate is desirably sensitized by a corona discharge as described in U.S. 2,588,699 to C. F. Carlson. The xerographic plate generally used comprises a film of amorphous selenium on a conductive backing, generally aluminum. Such a plate is relatively expensive but may be used thousands of times without damage. Accordingly, the per-copy cost of the xerographic print is relatively low. However, the extra handling cost involved in, first, developing the powder image on the xerographic plate and then transferring and fixing the image on a suitable lithographic plate and then cleaning the xerographic plate for reuse represents time and therefore cost consuming operations. In addition, the resolution lost in the transfer step inherent in the process together with the necessity of storing and paying for both lithographic and xerographic plates are objectionable. Accordingly, it has long been desired to use the xerographic plate itself as the lithographic plate.

The lithographic plate, as described, consists primarily of a finely-divided pigment dispersed in a hydrophilic adhesive. One type of xerographic plate long known to the art has the same physical structure. Such a plate is described in U.S. 2,663,636 to A. E. Middleton and comprises a photoconductive pigment dispersed in an insulating binder. A well known photoconductive material readily available at low cost is zinc oxide and is described in U.S. 2,169,840 to Lewis et al. Moreover, zinc oxide is a widely used paper coating pigment. Unfortunately, the requirements placed on the adhesives in xerography are diametrically opposed to the needs of the lithographic art.

Most pigments useful in forming binder plates, such as zinc oxide, zinc sulfide, lead oxide, etc. have resistivities which are too low to hold an electrostatic charge in the dark. Accordingly, the insulating properties of the resin used in preparing binder plates are highly critical, particularly when the binder-pigment composition is coated on a paper backing. In general, it has been found that using a hydrophilic resin as the binder in a xerographic plate apparently is sufficient to form a thin surface film of water and consequently lower the surface resistance so that there is considerable lateral leakage of the electrostatic charge. Such a plate is unable to hold an electrostatic latent image. Although xerographic binder plates have been available for many years, the only resins yet used commercially are silicone resins which are highly hydrophobic. Hence, before a xerographic binder plate can be utilized as a lithographic master, it is essential that the non-image areas of the plate be rendered hydrophilic.

A variety of means of accomplishing this have been investigated. One such method includes treating the non-image areas with a mixture of zinc acetate, water and ethyl alcohol. The thought was that in such a treatment the alcohol would soften or remove the surface film of silicone resin while the hydrophilic zinc acetate would deposit on the exposed zinc oxide to render the surface hydrophilic in a manner analogous to the action of fountain solutions. Attempts to print with a plate so treated have uniformly been unsuccessful, it being seldom possible to obtain printing runs of more than a dozen copies without the non-image areas inking up. Other methods were investigated, but were also unsuccessful.

There have now been discovered processes whereby excellent quality lithographic printing plates, suitable for

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long runs, may be prepared directly from a xerographic binder plate. In general, the invention comprises forming a binder plate of a photoconductive insulating oxide or sulfide and in particular of zinc oxide, zinc sulfide, cadmium sulfide, lead oxide, or mixtures or combinations containing these photoconductive pigments either with each other or with other photoconductive pigments such as mercuric sulfide, etc. in any resin having the requisite electrical properties for use in the xerographic process. A plate so prepared is utilized in the regular xerographic process to form thereon a powder image which is permanently affixed thereto as by heating.

The image-bearing xerographic plate is then immersed in a special treating solution for about 30 to 60 seconds. The treating solution comprises any water soluble ferrocyanide or ferricyanide, any acid at least as strong as acetic, and water. Optionally a water-soluble dichromate or chromate may be added if desired. The plate is then used in a lithographic press with a novel fountain solution containing an acid at least as strong as acetic, a water-soluble ferrocyanide or ferricyanide and a hygroscopic agent. Plates so prepared have been utilized in printing runs of over twenty thousand copies without appreciable deterioration of image quality in any respect.

The following examples are presented in illustration but not in limitation of the invention and it is to be understood that the invention is to be limited only by the appended claims.

Example 1

A xerographic plate was prepared containing 2.5 parts of zinc oxide to one part of a silicone resin obtained from the General Electric Company, sold under the trade name SR82. The zinc oxide and silicone with enough toluene to give suitable grinding viscosity were ball milled to obtain a uniform dispersion of zinc oxide in the resin solution. The resin-pigment mixture was then coated on an 0.006" thick aluminum sheet and dried for three days. The plate was sensitized using a corona charging unit obtained from the Haloid Company of Rochester, New York, under the trade name "XeroX" corona unit. The plate was then exposed to a line-copy image and developed using a magnetic brush and a xerographic toner comprising finely-divided gilsonite. The magnetic brush development process is described, for example, in U.S. patent application Ser. No. 562,845, filed on February 1, 1956, by Saul and Simmons, now U.S. Patent No. 2,791,949. The powder image was fixed to the plate by heating for 90 seconds in an oven at 290° F.

The plate so prepared was then dipped in a treating solution consisting of 0.5% (by weight) of sodium ferrocyanide; 0.2% (by volume) of glacial acetic acid; and 0.01% (by weight) of ammonium dichromate—the balance being water. The plate was immersed for a total time of 60 seconds. After removal from the treating solution the plate was rinsed with water and rubbed lightly with cotton dipped in a mixture of one volume of Platex (manufactured by Addressograph-Multigraph Corporation of Cleveland, Ohio) and two volumes of water. The composition of Platex is not known but it is believed to comprise a nickel salt, ammonium acid phosphate, butanal, cellulose gum, diethylene glycol, formaldehyde and water. The plate was then mounted on a lithographic press and wet with a fountain solution containing 0.1% (by weight) of sodium ferrocyanide; 0.05% (by volume) of glacial acetic acid; 1.0% (by weight) glycerine and the balance water. Six thousand prints were run off without deterioration of image quality.

Example 2

Example 1 was repeated excepting that the ammonium dichromate was omitted from the treating solution. Examination of the prints produced by the lithographic plates so prepared showed that the image dots, particularly the

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smaller dots, became water receptive and did not print satisfactorily.

Examples 3 and 4

Two lithographic plates were prepared and tested as in Example 1 except that in the treating solutions the amount of dichromate was 0.05% for Example 3 and 0.25% in Example 4. The image quality obtained in Example 3 was equivalent to that in Example 1. In Example 4 it was found that the random powder particles present in the non-image areas became ink receptive during printing causing a deleterious amount of background in non-image areas.

Examples 5 through 12

A series of eight lithographic plates were prepared and tested as in Example 1 except that the following acids were used in the treating solution in place of acetic acid: oxalic, tartaric, citric, tannic, hydrochloric, nitric, phosphoric and sulfuric acids. In each case the print quality was fully equivalent to that obtained in Example 1.

Examples 13 and 14

Lithographic plates were prepared and tested as in Example 1 except that in the treating solution for Example 13 potassium ferrocyanide was substituted for sodium ferrocyanide and in Example 14 calcium ferrocyanide was substituted for sodium ferrocyanide. In each case the image quality of the prints obtained from these plates were fully equivalent to the image quality obtained in Example 1.

Example 15

A lithographic plate was prepared and tested as in Example 1 except that potassium ferricyanide was used in place of sodium ferrocyanide. Prints obtained from this plate were equivalent to those obtained in Example 1. However, the plate had to be kept in the dark as under the influence of light zinc ferricyanide decomposes.

Examples 16 through 24

A series of nine lithographic plates were prepared and tested as in Example 1 except that the immersion time was varied as follows: 5 seconds; 15 seconds; 30 seconds; 45 seconds; 60 seconds; 240 seconds; 420 seconds; 540 seconds; 600 seconds. Plates immersed for 15, 30, 45 and 60 seconds gave prints of equivalent quality to those produced in Example 1. The remaining plates gave prints of poor quality and in the case of Example 24, no prints were obtainable as the coating sloughed off from the prolonged immersion.

Examples 25 through 28

A series of four lithographic plates were prepared and tested as in Example 1 except that in the treating solution the concentration of the acetic acid was varied as follows: 0.5%; 1%; 2% and 4% respectively. In each case the prints obtained from the lithographic plate so prepared were fully equivalent in quality to those prepared in Example 1.

Examples 29 through 35

A series of lithographic plates were prepared and tested as in Example 1 except that the ferrocyanide concentrations were as follows: 0.25%; 0.5%; 1%; 2%; 4%; 5% and 10%. In each case the immersion time was one minute. In each case the prints so produced were fully equivalent to those produced in Example 1.

Example 36

A lithographic plate was prepared and tested as in Example 1 except that a portion of the treating solution was used as the fountain solution. The image areas gradually became water receptive.

Example 37

A lithographic plate was prepared and tested as in Example 1 except that there was added to the fountain solution 0.002% ammonium dichromate. The non-image areas inked up slowly.

Examples 38 through 41

Four lithographic plates were prepared and tested as in Example 1 except that in the fountain solution the following concentrations of sodium ferrocyanide were used: 0.04%; 0.1%; 0.2%; and 0.5%. The plates used with the fountain solution containing 0.1%; 0.2% and 0.5% gave very good prints and long runs while the fountain solution containing only 0.04% sodium ferrocyanide was deemed inoperable.

Examples 42 and 43

Two lithographic plates were prepared and tested as in Example 1 except that the concentration of acetic acid in the fountain solution was increased to 0.08% and 0.2%, respectively. Again excellent results were obtained with both plates.

Example 44

A lithographic plate was prepared and tested as in Example 1 except that the zinc oxide coating contained 0.036% rose bengal dye. Prints obtained from the lithographic plate so prepared were fully equivalent to those obtained in Example 1.

It is believed that the reaction which occurs during immersion in the treating solution is a liberation of ions from the metallic oxide or sulfide due to the action of the acid thereon, followed by formation of an insoluble ferro-/or ferricyanide either by forming a simple metal ferro-/or ferricyanide or a complex ferro-/or ferricyanide as described, for example, by A. E. Williams in his book "Cyanogen Compounds," second edition, published by Edward Arnold Company, London, England, in 1948. Binder plates of the type used herein are well known to those skilled in the art and are described, for example, in U.S. Patent application Ser. No. 311,546, filed September 25, 1952, by A. E. Middleton et al., now abandoned.

The novel fountain solutions of the instant invention also contain a hygroscopic agent as commonly used in the art. A preferred hygroscopic agent is glycerine although other polyols known to those skilled in the art as hygroscopic agents may be used, i.e., ethylene glycol, propylene glycol, diethylene glycol, sorbitol, etc. Desirably, although not necessarily, the fountain solution contains a small amount of a suitable water-soluble protective colloid preferably cellulose gum (sodium carboxymethyl cellulose) although other water-soluble colloids such as sodium alginate, gluconic acid, polyvinyl alcohol, methyl cellulose, etc. may be used. The water-soluble colloid is believed to supplement the hygroscopic polyol in preventing drying of the planographic plate when a run is interrupted for some reason.

It is also desirable to add a small amount of a water-soluble aldehyde to the fountain solution to inhibit mold growth and reduce any tendency of the ink roll on the lithographic press from becoming objectionably tacky. It

is preferred to use formaldehyde by reason of its low cost, but other water-soluble aldehydes such as glyoxal, furfuraldehyde, acetaldehyde, etc. may be used.

While the present invention has been described herein as carried out in specific embodiments thereof, it is not desired to be limited thereby but it is intended to cover the invention broadly within the spirit and scope of the appended claims.

I claim:

1. The improvement in the art of printing from planographic printing plates whose non-printing areas contain a water-insoluble ferrocyanide which comprises the step of treating the non-printing areas of the plate with an aqueous solution of from about 0.1 to 0.5% (by weight) of a water-soluble ferrocyanide, an acid in a concentration to give said solution a hydronium ion concentration equal to that provided by a solution of from 0.05% to 0.2% (by volume) of glacial acetic acid, a water-soluble aldehyde, a water-miscible polyol and a water-soluble protective colloid.

2. The improvement in the art of printing from planographic printing plates whose non-printing areas contain a water-insoluble ferrocyanide which comprises the step of treating the non-printing areas of the plate with an aqueous solution of from about 0.1 to 0.5% (by weight) of a water soluble ferrocyanide, an acid in a concentration to give said solution a hydronium ion concentration equal to that provided by a solution of from 0.05% to 0.2% (by volume) of glacial acetic acid, formaldehyde, glycerin, and cellulose gum.

3. The improvement in the art of printing from planographic printing plates whose non-printing areas contain a water-insoluble ferrocyanide which comprises the step of treating the non-printing areas of the plate with an aqueous solution of from about 0.1 to 0.5% (by weight) of a water-soluble ferrocyanide, an acid in a concentration to give said solution a hydronium ion concentration equal to that provided by a solution of from 0.05% to 0.2% (by volume) of glacial acetic acid, formaldehyde, a water-miscible glycol, and cellulose gum.

4. The improvement in the art of printing from planographic printing plates whose non-printing areas contain a water-insoluble ferrocyanide which comprises the step of treating the non-printing areas of the plate with an aqueous solution comprising from about 0.1 to 0.5% by weight of a water-soluble ferrocyanide and an acid in a concentration to give said solution a hydronium ion concentration equal to that provided by a solution of from about 0.05% to 0.2% by volume of glacial acetic acid.

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