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PROCESS FOR DELETING LITHOGRAPHIC IMAGES

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This invention concerns a deletion fluid and a process of using the deletion fluid to delete printing areas from a lithographic plate comprising an oleophilic oxidized image area in hardened colloid.

In one method of preparing lithographic printing plates photographically, as described in Yackel and Abbott, U.S. Patent No. 3,146,104, issued Aug. 25, 1964, a developable silver halide image is formed by means of exposure to a line or half-tone subject in a hardened hydrophilic organic colloid-silver halide emulsion such as a gelatino-silver halide emulsion.

Development is carried out using a polyhydroxybenzene silver halide developer, which is either present in the emulsion or a layer effectively adjacent thereto. When the developer is oxidized in the development reaction in the presence of the hydrophilic organic colloid vehicle present in the silver halide emulsion layer, an oleophilic image is formed. Upon inking the moistened plate with a greasy ink and printing in a lithographic printing press the desired lithographic reproduction, which is negative to the original subject is obtained.

If, however, a positive working plate is desired, the photographic element described above may contain, in addition, a fogged silver halide emulsion as the uppermost layer. When this photographic element is exposed to a subject, and its contigous silver halide developing agent activated, the developing agent reacts with the sensitive lower silver halide emultion layer to form the negative image, and the unused silver halide developing agent present in the unexposed areas of the sensitive lower silver halide emulsion layer then migrates upward to the fogged silver halide emulsion layer and, when oxidized in the presence of a hydrophilic organic colloid present in this layer, forms an oleophilic image in the surface which is positive in respect to the original subject.

Occasionally it is desirable to delete part of the image on the lithographic plate prepared as above without affecting the remaining areas. Moreover, it has been desirable to delete areas from a plate which has completed a partial run so that the plate with the modified image can then be used to make additional copies with the undeleted areas unaffected.

Many agents have been applied to lithographic plates prepared as above in an attempt to delete the image. Among these have been metal salts, gums, latexes, gelatin, dichromate bleaches, and silica. None of these treatments permanently remove the image without producing other effects such as press contamination, etc. Mechanical means, such as rubbing the undesired image area with fine steel wool, have also been unsatisfactory.

I have found that an aqueous solution containing ferricyanide ions or ferrocyanide ions can be used to delete the image on the processed photographic lithographic plate.

One object of this invention is to provide a deletion solution for use in deleting the image from a photographic lithographic plate comprising a tanned image area in hardened colloid. An additional object is to provide a process for deleting the image from a photographic lithographic plate comprising a tanned image area in hardened colloid. An additional object is to provide a

method of deleting an image from a hardened gelatin colloid layer containing therein oleophilic pigment by means of a ferricyanide or ferrocyanide deletion solution.

The above objects are attained by treating the surface of the plate with a solution of at least 2 percent ferricyanide ion, for example, water-soluble salts such as potassium, sodium, ammonium, etc. The useful range is from 2 to 8 percent. Much larger concentrations can be used with good deletion, but there is no advantage in using the larger amount.

Ferrocyanide ions may also be used, for example, the water-soluble salts such as potassium, sodium, ammonium, etc. However, it is preferred that a solution of at least 8 percent ferrocyanide be used.

It will be appreciated that the ferricyande and ferrocyanide ions are preferably in the form of water-soluble salts such as the potassium or sodium salts. However, other water-soluble salts may be used which release the ferricyanide or ferrocyanide ions in aqueous solution. It will also be appreciated that the deletion fluid may contain other components such as thickener, and the like, provided these components do not react adversely with the ferricyanide or ferrocyanide ions. Suitable thickeners include hydrophilic organic colloids such as, for example, gelatin, hydroxyethyl cellulose, carboxymethyl cellulose, starch, guar gum, etc.

The deletion fluid may be applied by a swab, brush, quill, sponge, or by other means which will provide for delineating the area to be deleted. If prepared in a viscous form, it may be squeezed from a compressible tube. Although it is preferable that the deletion fluid be applied to the moist plate, it can be applied to a plate which is in a dried-down condition.

The following examples are intended to illustrate the practice of my invention but not to limit in any way.

Example 1

A 7 percent solution of potassium ferricyanide was applied to a lithographic plate prepared as follows according to Yackel et al. U.S. patent application, Serial No. 861,125, filed December 21, 1959.

A photographic emulsion was prepared by combining the following ingredients:

I. Fine grain silver chloride emulsion containing:
1 mole of Ag per 4350 cc. ---------- g-- 43.5

II. Paraffin dispersion prepared as follows:
80 g. molten paraffin dispersed in 400 cc. 10% photographic gelatin solution containing 5 cc. of 10% Alkanol B (propylated naphthalene sulfonate) solution ---------- g-- 10.0

III. 4-phenyl catechol dispersion prepared as follows:
50 g. 4-phenyl catechol dissolved in 100 cc. dibutylphthalate at 60–70° C. dispersed in 500 cc. 10% photographic gelatin and 50 cc. 7½% saponin solution and passed through the colloid mill five times ---------- g-- 10.0
15% saponin solution ---------- g-- 1.0
10% formaldehyde solution ---------- g-- 1.0
Water ---------- cc-- 20.0

The emulsion was coated 6.5 grams per square foot on a film base and dried.

The film was exposed to a line negative, then activated for 20 seconds in a 4 percent solution of sodium carbonate monohydrate. Thereafter, the plate was bathed in a phosphoric acid solution, placed in a lithographic printing press, inked in the conventional manner and 40 good copies printed.

The plate was removed from the lithographic printing press and a 7 percent solution of potassium ferricyanide

was applied to the areas to be deleted on the wet plate. The solution was allowed to stand for five seconds, wiped to remove any excess deletion fluid and replaced in the lithographic printing press. The areas treated with the deletion fluid now appeared to be hydrophilic and would not print. Ten additional good copies were printed of the areas which had not been treated with deletion fluid. No adverse effects were observed in the non-deleted areas or in the fountain solution.

Example 2

Other embodiments employing a hardened colloid layer containing an oleophilic tanned image are also treated with the deletion fluid with satisfactory results. These include those of the positive-positive process, wherein the developer is in a layer under the silver halide emulsion and wherein a fogged silver halide emulsion is coated over the positive-negative element, as well as those wherein the image is obtained by the diffusion transfer process, by the colloid transfer process, etc. In each instance, the lithographic plate carries a gelatin layer which contains oxidation agents which render the gelatin oleophilic in the image area and the gelatin has a hardness equivaletnt to that of a gelatin layer containing from 2 grams to about 15 grams of dry formaldehyde per pound of gelatin.

Example 3

Lithographic plates prepared as in Example 1 were taken off the lithographic press after having made 40 good copies and subjected to treatment as in Example 1. Commercial bleach comprising a bichromate-sulfuric acid combination gave bad toning. Colloidal silica in an aqueous suspension resulted in deleting the image temporarily but it returned after several prints. Excess silica builds up in the fountain, causing an obliteration of the complete image on the plate and contaminating the press. Commercially available sodium hypochlorite not only did not remove the image area treated but rendered this area ink receptive. Sodium hydroxide resulted in complete obliteration of the plate surface. Metal salts, gelatin and tannic acid were also unsuccessful.

It will be appreciated that the support on which the lithographic plate is coated is not critical and that any of the customary supports used for lithographic plates can be used. Moreover, the components of the sensitive elements of the lithographic plate can be varied appreciably in the known photographic silver halide emulsions such as silver chloride, silver bromide, silver iodide, silver bromochloride, silver bromoiodide, and silver bromochloroiodide emulsions. Direct positive emulsions may be used such as solarized emulsions, e.g. of the Leermaker U.S. Patent 2,184,013 etc.

A variety of hydrophilic organic colloid vehicles can be used for the silver halide emulsions for making the plate. Proteins such as gelatin, soy bean protein, casein, as well as synthetic organic colloids which are hydrophilic, such as polyvinyl alcohol, hydrolyzed cellulose esters, etc., may be used to the extent that they form the desired oleophilic image with the oxidized developing agent in the development reaction.

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.

I claim:

1. A process for rendering hydrophilic an image area on a lithographic printing plate comprising a support having thereon a top layer comprising gelatin having a hardness equivalent to that of a gelatin layer containing from 2 grams to about 15 grams of dry formaldehyde per pound of gelatin and containing in the gelatin layer an oleophilic tanned gelatin silver image area, obtained by developing an exposed silver halide emulsion with a polyhydroxy benzene silver halide developing agent, comprising forming a silver salt by imbibing into the image area to be rendered hydrophilic an aqueous solution consisting essentially of ions selected from the class consisting of ferricyanide and ferrocyanide.

2. A process for rendering hydrophilic an image area on a lithographic printing plate comprising a support having thereon a top layer comprising gelatin having a hardness equivalent to that of a gelatin layer containing from 2 grams to about 15 grams of dry formaldehyde per pound of gelatin and containing in the gelatin layer an oleophilic tanned galatin silver image area, obtained by developing an exposed silver halide emulsion with a polyhydroxy benzene silver halide developing agent, comprising forming a silver salt by imbibing into the image area to be rendered hydrophilic an aqueous solution consisting essentially of an alkali metal ferricyanide.

3. A process for rendering hydrophilic an image area on a lithographic printing plate comprising a support having thereon a top layer comprising gelatin having a hardness equivalent to that of a gelatin layer containing from 2 grams to about 15 grams of dry formaldehyde per pound of gelatin and containing in the gelatin layer an oleophilic tanned gelatin silver image area, obtained by developing an exposed silver halide emulsion with a polyhydroxy benzene silver halide developing agent, comprising forming a silver salt by imbibing into the image area to be rendered hydrophilic an aqueous solution consisting essentially of an alkali metal ferrocyanide.

4. A process for rendering hydrophlic an image area on a lithographic printing plate comprising a support having thereon a top layer comprising gelatin having a hardness equivalent to that of a gelatin layer containing from 2 grams to about 15 grams of dry formaldehyde per pound of gelatin and containing in the gelatin layer an oleophilic tanned gelatin silver image area, obtained by developing an exposed silver halide emulsion with a polyhydroxy benzene silver halide developing agent, comprising forming a silver salt by imbibing into the image area to be rendered hydrophilic an aqueous solution consisting essentially of potassium ferricyanide.

5. A process for rendering hydrophilic an image area on a lithographic printing plate comprising a support having thereon a top layer comprising gelatin having a hardness equivalent to that of a gelatin layer containing from 2 grams to about 15 grams of dry formaldehyde per pound of gelatin and containing in the gelatin layer an oleophilic tanned gelatin silver image area, obtained by developing an exposed silver halide emulsion with a polyhydroxy benzene silver halide developing agent, comprising forming a silver salt by imbibing into the image area to be rendered hydrophilic an aqueous solution consisting essentially of potassium ferrocyanide.

6. A process for rendering hydrophilic an image area on a lithographic printing plate comprising a support having thereon a top layer comprising gelatin having a hardness equivalent to that of a gelatin layer containing from 2 grams to about 15 grams of dry formaldehyde per pound of gelatin and containing in the gelatin layer an oleophilic tanned gelatin silver image area, obtained by developing an exposed silver halide emulsion with a polyhydroxy benzene silver halide developing agent, comprising forming a silver salt by imbibing into the image area to be rendered hydrophilic an aqueous solution containing at least 2 percent alkali metal ferricyanide, the balance being water and hydrophilic colloid thickeners.

7. A process for rendering hydrophilic an image area on a lithographic printing plate comprising a support having thereon a top layer comprising gelatin having a hardness equivalent to that of a gelatin layer containing from 2 grams to about 15 grams of dry formaldehyde per pound of gelatin and containing in the gelatin layer an oleophilic tanned gelatin silver image area, obtained by developing an exposed silver halide emulsion with a polyhydroxy

benzene silver halide developing agent, comprising forming a silver salt by imbibing into the image area to be rendered hydrophilic an aqueous solution containing at least 8 percent alkali metal ferrocyanide, the balance being water and hydrophilic colloid thickeners.

8. A process for rendering hydrophilic an image area on a lithographic printing plate comprising a support having thereon a top layer comprising gelatin having a hardness equivalent to that of a gelatin layer containing from 2 grams to about 15 grams of dry formaldehyde per pound of gelatin and containing in the gelatin layer an oleophilic tanned gelatin silver image area, obtained by developing an exposed silver halide emulsion with a polyhydroxy benzene silver halide developing agent, comprising forming a silver salt by imbibing into the image area

to be rendered hydrophilic a viscous solution consisting essentially of a hydrophilic colloid thickener and ions selected from the class consisting of ferricyanide and ferrocyanide.

References Cited by the Examiner

UNITED STATES PATENTS

2,013,116	10/1930	Troland.	
2,988,988	6/1961	Kurz	101—149.2
3,113,023	12/1963	Mellan	96—33
3,146,104	8/1964	Yackel et al.	101—149.2 X

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