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LITHOGRAPHIC PLATE, ITS PREPARATION AND TREATMENT SOLUTION THEREFOR

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This invention relates to lithography and more particularly to specially treated coated and uncoated lithographic plates, their preparation through the use of an organic complexing or chelating agent and to the treatment solutions therefor.

Lithographic plates having a conventional bichromated coating suffer from the inherent disadvantage that they undergo what is known as the "dark reaction" after the lithographic plate is coated with the bichromate. This "dark reaction" is a progressive hardening or insolubilization of the coating film in the absence of light and it has the detrimental effect of causing overall pre-exposure or fogging of the plate. If the "dark reaction" is allowed to progress too far, there is such a small difference in solubility between the exposed and unexposed coating that a satisfactory image cannot be produced during the subsequent development step. There are a number of factors which affect the rate of the "dark reaction." The important ones are the moisture content of the dried coating, the pH value of the dried coating, the ambient temperature conditions and the presence of polyvalent ions.

Those investigators working in this field are aware of the first three factors but there is little or no information in the literature or industry regarding the fourth factor. The first and third of these factors result directly from the operating conditions of the particular lithographic plant and are not susceptible of being controlled easily. A variation in the pH value of the dried coating affects the photographic sensitivity of the coating and is therefore undesirable. The fourth factor is the special subject of the present invention as it has been found that the elimination of polyvalent ions can be achieved by a special treatment of the metal plate prior to coating with an organic complexing or chelating agent.

It is an object of this invention to eliminate or very substantially eliminate the presence of polyvalent ions by treating the lithographic plate with an organic complexing agent which effects chelation of the polyvalent metal ions.

Another object of the invention resides in eliminating or suppressing ionization arising either from the lithographic metal plate or from the bichromated coating and to cause chelation of both types of polyvalent metal ions.

A further and more specific object of the invention resides in the treatment of an aluminum or zinc lithographic plate with the sodium salt of ethylene diamine tetra acetic acid or certain other hereinafter mentioned chelating agent treatment solutions in order to inhibit the "dark reaction."

Other and further objects and advantages will be understood or appreciated by those skilled in this art or will be apparent or pointed out hereinafter.

The "dark reaction" is an undesirable and difficultly controllable phenomenon which inherently proceeds during the preparation of lithographic plates using aluminum or zinc support plates which are coated with a bichromated colloid. This "dark reaction" results from polyvalent metal ions which have two main sources. The primary source is the metal plate itself. The secondary source is the bichromated coating which contains hexavalent chromium ions together with an organic colloid which acts as a reducing agent. This causes trivalent chromium ions to be released into the coating at the expense of the hexavalent chromium ions and it is the trivalent chromium ions which are responsible for the insolubilization of the

colloid in the bichromated coating due to a complex cross linking reaction.

The released trivalent chromium ions have the same insolubilizing effect on the colloid although at a slower rate as the flood of trivalent chromium ions released during the exposure of the bichromated coating to a light source rich in ultra-violet rays. The conversion of hexavalent chromium ions to trivalent chromium ions during the "dark reaction" is promoted by the presence of reducing agents. The aluminum and zinc metal of the plates themselves act as reducing agents and thus promote the "dark reaction" when they are coated with a bichromated colloid such as bichromated gum arabic.

According to the present invention, the aluminum or zinc metal plate is treated with a special treatment solution to inhibit or suppress the polyvalent metal ions from either source and thus the treated plate prevents reaction between the metal of the plate and the bichromated coating as well as eliminating the polyvalent metal ions arising from the plate itself during treatment.

It has been found that the treatment of the lithographic metal plate in situ prior to the coating operation produces a printing plate which is vastly superior in many respects to a conventional printing plate. One of the important advantages is that the "dark reaction" is inhibited for a period of at least several days.

Another advantage is the ease with which the bichromated coating can be flowed onto the metal plate thereby providing a more uniform film of the dried coating on the plate. An additional advantage is that the stripping or removal of the light-hardened deep etch stencil is greatly facilitated. A still further advantage is that the metal plate surface is cleaned more efficiently of oleophilic material as compared with a conventional weakly acidic counter etch. A further advantage resides in the fact that the unexposed portions of the bichromated casein or albumen plate surface releases much more easily during the development step as compared with a conventional bichromated aluminum or zinc lithographic plate. In effect, the use of the treatment solution on the lithographic plate prior to coating thereof eliminates polyvalent metal ions. Due to a complexing action the chelating agent not only suppresses the polyvalent metal ions originating from the lithographic plate metal itself but also prevents the trivalent chromium ions from reacting with the coating colloid without, however, adversely affecting the photographic sensitivity of the coating. Lithographic plates treated in accordance with this invention have the important advantage that the bichromated coating flows onto a thus treated plate with less difficulty and greater uniformity than on an untreated plate due to the fact that the pretreatment of the plate produces a very uniform chemical surface on the plate.

Because of the fact that a metal lithographic plate treated with a chelating agent inhibits cross linking of the colloid the subsequent stripping of the exposed bichromated coating is facilitated.

In carrying out the invention, the preferred procedure is to substitute the treatment solution for the conventional acidic counter etch. Accordingly, the aluminum or zinc plate is washed with water to remove excess soil and then flushed with the treatment solution for approximately 30 seconds while lightly scrubbing the plate with a bristle brush to remove imbedded soil. The plate is then rinsed with tap water and coated in the normal manner with the desired bichromated colloid.

It is not absolutely essential, however, to follow the above procedure since the treatment solution can also be successfully applied to the lithographic plate by dipping the plate in the treatment solution for several minutes and then rinsing with water and air drying. Plates pre-

pared in this manner have the same advantages as the plates resulting from the preferred procedure.

The treatment solution consists of an aqueous solution of the sodium salt of ethylene diamine tetra acetic acid having the following composition:

Ethylene diamine tetra acetic acid (99%)	grams	6.62
Sodium hydroxide (76% Na_2O)	grams	9.54
Water	ml	3,780

The composition of the treatment solution is critical or of critical significance in that the proportions of components can be varied by not more than 20% without appreciably or adversely affecting the working properties of the solution. If, however, the components are varied appreciably more than 20% the results of the invention are not obtainable. For example, if the sodium hydroxide is increased more than 20% the photographic sensitivity of the bichromated coating is adversely affected, whereas a decrease in the sodium hydroxide of more than 20% below the proportion given means that the treatment solution must be kept in contact with the plate for an excessive period of time during counter etching. If the ethylene diamine tetra acetic acid is increased appreciably more than 20% there is again an excessive contact time required between the plate and the solution whereas a decrease in this component or more than 20% adversely affects the photographic sensitivity of the bichromated coating. The water content is also critical because an increase thereof beyond 20% gives rise to an excessive contact time between the plate and the solution and a reduction of the water content of more than 20% causes the plate to be attacked by the solution with consequent etching.

It will thus be seen that the treatment solution must be strictly controlled as to its composition and proportions of components.

It has further been found that while the abovementioned treatment solution and its permissible variants in percentage composition is the most effective for inhibiting the "dark reacton," there are certain other solutions of polyhydroxycarboxylic acids or alkaline solutions of their salts which are successfully utilizable. These other treatment solutions are not quite as effective or as desirable as the preferred treatment solution set forth above but they do satisfactorily inhibit the "dark reaction" although to a somewhat lesser extent than the sodium salt of ethylene diamine tetra acetic acid. These other treatment solutions are as follows:

(1) An aqueous solution of the sodium salt of hydroxyethyl ethylene diamine triacetic acid of the following composition:

Hydroxyethyl ethylene diamine triacetic acid (98%)	grams	6.62
Sodium hydroxide (76% Na_2O)	grams	9.54
Water	mls	3,780

The composition of this solution cannot be varied by more than 20% without adversely affecting its working properties in exactly the same manner as the preferred treatment solution.

(2) An aqueous solution of sodium gluconate adjusted to pH 12 with sodium hydroxide and having the following composition:

Sodium gluconate	grams	100
Sodium hydroxide (76% Na_2O)	grams	3
Water	mls	1,900

The composition of this solution also cannot be varied by more than 20% for reasons set forth above.

(3) An aqueous solution of "sodium citrate" adjusted to pH 12 with sodium hydroxide and having the following composition:

Citric acid	grams	100
Sodium hydroxide (76% Na_2O)	grams	58
Water	mls	1,900

This composition cannot be varied by more than 20% for the same reasons already set forth.

(4) An aqueous solution of "sodium tartrate" adjusted to pH 12 with sodium hydroxide and having the following composition:

Tartaric acid	grams	100
Sodium hydroxide (76% Na_2O)	grams	54.6
Water	mls	1,900

Variations of more than 20% have adverse effects, the same as in the above treatment solutions.

(5) An aqueous solution of citric acid.

(6) An aqueous solution of tartaric acid.

The solutions 5 and 6 contain 5% by weight of the acids. Solutions appreciably more dilute than 5% require unusually long treatment periods but solutions of a strength greater than 5% work satisfactorily. These two solutions thus have the special advantage that they do not have a narrow critical working range.

The criticality of the treament solutions is emphasized by the fact that certain other treatment solutions which were tried did not work successfully as replacements for the sodium salt of ethylene diamine tetra acetic acid or the other operable treatment solutions mentioned just above.

The unsuccessful solutions of 10% concentration were as follows:

(1) An aqueous solution of tetra sodium pyrophosphate ($Na_4P_2O_7$);

(2) An aqueous solution of sodium tetraphosphate $Na_6P_4O_{13}$; and

(3) An aqueous solution of tri-sodium phosphate.

(4) An aqueous solution of sodium tri-polyphosphate ($Na_5P_3O_{10}$).

The fact that certain solutions did not work successfully make it all the more surprising and unexpected that the operable treatment solutions produced such excellent results. The explanation for this is not fully known or understood at this time.

It is further understood that the invention is applicable both to surface and to deep etch lithographic plates, both types being well-known in lithography.

What is claimed is:

1. A lithographic plate composed of a metal selected from the group consisting of aluminum and zinc the surface of which has been treated with a solution of the following components in the following relative proportions:

Ethylene diamine tetraacetic acid	grams	6.62
Sodium hydroxide	grams	9.54
Water	milliliters	3,780

in which solution each of the components can be varied only within ±20% of the stated quantity, rinsed and then coated with a conventional bichromated colloid, thereby preventing reaction between the plate metal and the bichromated colloid and inhibiting polyvalent metal ions during preparation of the lithographic plate.

2. A method of preparing a lithographic plate free from "dark reaction" which comprises treating the surface of a metal plate selected from the group consisting of aluminum and zinc with a solution of the following components in the following relative proportions:

Ethylene diamine tetraacetic acid	grams	6.62
Sodium hydroxide	grams	9.54
Water	milliliters	3,780

in which solution each of the components can be varied only within ±20% of the stated quantity, rinsing the thus treated plate and then coating it with a conventional bichromated colloid, thereby preventing reaction between the plate metal and the bichromated colloid and inhibiting polyvalent metal ions during preparation of the lithographic plate.

(References on following page)

References Cited by the Examiner

UNITED STATES PATENTS

2,168,181	8/1939	Ulrich	260—534
2,265,829	12/1941	Wood	101—149.2 X
2,374,070	4/1945	Barensfield	101—149.2
2,379,646	7/1945	Mueller.	
2,399,208	4/1946	Coolidge	96—93 X
2,582,347	1/1952	Newman	101—149.2
2,764,085	9/1956	Shoemaker et al.	96—33 X
2,922,715	1/1960	Gumbinner	96—86 X
2,942,974	6/1960	Schwarz	96—33
2,946,683	7/1960	Mellan et al.	96—33 X
2,950,195	8/1960	Hodgins et al.	96—93

3,016,297	1/1962	Mochel et al.	96—86
3,033,214	5/1962	Bersworth et al.	260—534

OTHER REFERENCES

Chemistry of Lithography, Lithographic Technical Foundation, New York, 1952, pp. 85, 92, 93, 102–109, 117–122.

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