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PRINTING PLATE

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My invention relates to printing and particularly to a new type of photo-lithographic printing plate or master having thereon a printing image of metal or metal oxides characterized by its exceptional durability and long life.

The photo-lithographic processes now generally used for printing on paper, metal, leather and the like involve the use of a photo-lithographic plate of zinc or aluminum, certain portions of which bearing the image to be printed are sensitive or receptive to printing ink while the other, non-printing surfaces are insensitive to ink. Printing from such plates may be done either by the direct or offset method. In the direct method the paper or other material is brought into contact with the inked plate while in the offset method an inked image is first transferred from the lithographic plate to a roller and thence to the paper or other material as the roller is brought into contact therewith.

In order to fix the image on the plate the surface of the plate is first grained and then coated with a light-sensitive composition usually consisting of a solution of albumen or gelatine with a dichromate, and dried. The image is then formed in this light-sensitive coating by exposing it to the light of an electric arc or other source of ultra violet light passing through a photographic negative in contact with the coating. The coating is initially soluble in water but those portions thereof which are exposed to the ultra violet light become insoluble or hardened. A so-called developing ink is applied to the plate after the exposure and the plate is developed by washing. The soluble portions of the coating with the ink layer thereon are removed by the water leaving only the insoluble portions with the superposed ink. In printing from such plates the non-printing areas are desensitized or made grease-resisting so that they will attract and hold water and thus repel ink.

The printing image on such plates obviously consists only of the film of albumen dichromate and depends entirely for its integrity on the adherence of the film to the surface of the steel. Due to the structural weakness of such an image it is easily damaged and the number of printed copies that can be made therefrom is limited.

I have discovered a method of making a printing plate of this general type wherein the printing image is formed of metal or metal oxides which are not only more resistant to damage than the ordinary albumen dichromate films but which are more susceptible to ink than any albumen image, are capable of reproducing finer details, and which are substantially indestructible when given ordinary care.

My plates are formed of alloy steel containing at least 6%, by weight, of chromium, and preferably, containing chromium in such quantities (12% and up) as will render the steels substantially stainless. The presence or absence of other elements in the alloy, such as copper, molybdenum, nickel, silicon and the other elements ordinarily used in stainless steels, is immaterial and any such elements may be present in the quantities usually encountered in steels of this character.

The plates are first grained by any of the well-known processes and a film of dark colored oxides is formed in and substantially integral with the grained surface by treating the plate in a solution of sulphuric acid, water and a second acid selected from the group consisting of chromic, vanadic, metavanadic, manganic and permanganic. However, I prefer to use a solution of sulphuric acid, water and chromic acid which may be formed by adding any of the chromates or dichromates, preferably sodium dichromate, to a solution of sulphuric acid and water. The reaction forms chromic acid and a sulfate or bisulfate of the chromate or dichromate-forming element. Small quantities of iron sulfate or chromium sulfate, or both, added to the solution facilitate the coloring, and a solution which will show upon analysis the following ingredients within the proportions stated may be used:

	Per cent by weight
Water	35–55
Free sulphuric acid (1.84 sp. gr.)	15–55
Chromic, vanadic, metavanadic, manganic or permanganic acid	2–20
Iron sulfate	0.01–10
Chromium sulfate	0.01–10
Other sulfates or bisulfates and impurities	Balance

My preferred solution, in which the chromic acid is formed from sodium dichromate, will show upon analysis the following ingredients in about the proportions stated—

	Percent by weight
Water	40–50
Free sulphuric acid (1.84 sp. gr.)	30–50
Chromic acid	6–10
Iron sulfate	0.1–1
Chromium sulfate	1–2
Sodium sulfate or bisulfate and impurities	Balance

The solution is preferably heated to a temperature of about 180° to 220° F. and the steel is simply immersed therein until a film of dark colored oxide is formed in and substantially integral with the grained surface of the steel. The time required varies quite widely with the analysis of the steel and with the temperature of the solution. Within the preferred temperature range the coloring time, depending upon the analysis and the passivity of the ball grained surface, may vary from 30 minutes to 2 hours. The treatment should be continued until a dark colored film is formed although the particular color is not of importance. Blacks, blues, greens and maroons may appear.

It is to be understood that in commercial practice the printer would undoubtedly be supplied with grained plates colored as above described and ready for his use.

Starting with such a pre-grained and pre-colored plate the colored surface of which is slightly porous and very sensitive to printing ink, the printing image may be imparted thereto either by ink transfer from another image or by printing it directly thereon from a negative or positive in the same way that images are imparted to a zinc or aluminum plate through the medium of a light-sensitive coating. For example, the image may be printed in etching ink upon the colored plate in an offset press or by hand transfer. A resist of any suitable material is next applied to the image. As a resist, I prefer first to brush lightly over the inked image a film of finely powdered asphalt and then to cover the asphalt with finely powdered French chalk. The powdered material adheres to the inked image but will not adhere to the other portions of the plate. The plate with the powdered asphalt and chalk thereon is then heated to fuse or melt the asphalt into the ink image. No special degree of heat is necessary except that it must be sufficient to fuse the asphalt.

Certain inks such as "high resin" or "varnish" inks, when dry, form a satisfactory resist in and of themselves, and where the image can be printed in such inks no asphalt-chalk resist is necessary.

The plate with the resist covered image thereon is then subjected to an electrolytic treatment which will strip off all of the exposed colored oxides. This can be accomplished by treating the plate as anode in almost any electrolyte which will not detrimentally affect either the surface of the steel or the functioning of the resist. For example, if it is desired to preserve the grained surface of the steel in the non-printing areas which is usually the case, the electrolyte shoud be such as will remove the color without injury to the graining. On the other hand, if the non-printing areas of the plate are to be etched to a depth below the level of the printing surface, then the electrolyte need only be such as will not destroy the resist.

Examples of satisfactory electrolytes are as follows: a water solution containing 10% nitric acid and 5% hydrochloric acid; a solution of ordinary household lye containing approximately 75 grams per liter of water; a solution containing 75 grams of sodium nitrate per liter of water; a solution containing 70% phosphoric acid and 30% sulphuric acid with a small quantity of citric acid dissolved therein; and 85% phosphoric acid solution. Where a bath such as is used to color the steel is conveniently available it may be used as an electrolyte to remove the colored oxides. Electrolytes at room temperature work very well although higher temperatures, provided they are not so high as to soften or remove the resist, may be employed. Violent evolution of gas from the surface of the colored steel may remove the resist, particularly at the edges, and therefore the current density employed should be kept low enough to avoid this. As a general rule it may be said that with most electrolytes a current density of about 1 ampere per sq. in. of film to be removed will produce satisfactory results.

However, the proper current density and the duration of the treatment in any electrolyte can be easily determined by gradually increasing the current until the surface (colored oxides) of the anode begin to grow light in color. Current is then permitted to flow at this amperage until the oxide film is removed or becomes easily removable by light rubbing.

After the removal of the colored oxides from the non-printing areas the resist and ink may be removed from the printing areas by any of the common solvents leaving the printing plate with the printing image thereon consisting only of the colored oxides which are oxides or hydrated oxides of the alloying elements in the steel.

The plate is then ready for the printer and may be worked up on the press in exactly the same manner as a plate bearing an albumen image. The colored oxides are very sensitive to ink and are capable of carrying much more "rolled on" ink than the old type of albumen image. Furthermore, the image, instead of being merely stuck on the steel as is the case with an albumen image is actually in and substantially integral with the steel itself.

It is clear, of course, that a plate made in this way must be considered as a "transfer" plate because the image is produced by printing methods from a plate already produced. There are, however, many occasions in the printing industry where it is necessary to have several plates of the same kind. As made by the usual methods, transfer plates can be used to produce only a limited number of lithographic prints before the plate starts to break down. My transfer plates, however, are characterized by an exceptionally long printing life because the ink sensitive image which is formed entirely of oxides of iron, chromium, nickel and other alloying elements in the steel is substantially indestructible when subjected to ordinary care and normal use.

Where no plate is available from which a transfer can be made the image may be formed on my plate by the ordinary photographic methods now used. A light-sensitive film of albumen dichromate or other material, such as gelatine or asphalt, may be applied to my pre-grained and pre-colored plate by the usual methods well understood in the art and the image imparted to such film by means of printing from a photographic screen negative or positive, as may be required. Due to the porosity of the oxide color film the light hardened albumen image is anchored to the plate by being partially absorbed in the oxide film. A developing ink is applied, rubbed down, and the plate developed by washing in the usual manner which will of course remove the soluble albumen layer and the developing ink from the non-printing areas leaving the insoluble image-forming albumen in the printing areas. The image is then inked up and a resist such as powdered asphalt and French chalk applied thereto and heat hardened as above described, or if a high

resin or varnish ink is used, the ink itself, when dry, will form a satisfactory resist. The plate may then be anodically treated as described above to remove the colored oxides from the non-printing areas of the plate; the insoluble albumen with the overlying resist preventing the removal of the colored oxides from the printing areas. The resist can be then removed with a suitable solvent and, if desired, the albumen image may also be effectively removed by gently scrubbing with a solution of caustic soda although it may be permitted to wear off in use. In many types of printing which do not require the ultimate in printed detail it is not necessary to remove the light hardened albumen dichromate overlying the oxide image although for the finest type of work superior results are attained by removing it because the oxide film on my plate is substantially more sensitive to the reception of lithographing ink than the albumen dichromate and, due to its exceptional durability will remain so throughout prolonged printing operations.

Where it is desired to produce a deep-etched plate the light sensitive albumen dichromate or other coating is hardened on the metal oxide layer in the non-printing areas. A developing ink is applied and the plate developed in the usual way. The plate may then be inked up with a high resin or varnish ink to form a resist or the resist may be formed from powdered asphalt and French chalk, as described above, on surfaces which have been inked with ordinary lithographing ink. The oxide color on the exposed areas of the plate is then removed by an electrolytic treatment, as described above, and the plate etched by immersion in a normal temperature solution of iron perchloride preferably of from 38 to 42° Baumé. By immersion for about 15 minutes in iron perchloride the exposed areas of the plate may be etched to a depth of about 3 thousandths of an inch which is considerably in excess of the depth to which plates of the present type can be deep-etched. In order that the plate may be etched uniformly the solution should be kept agitated by a current of air or other suitable means.

Where it is desired to produce a plate in which the printing areas are in relief above the non-printing areas the resist is of course applied to the printing areas, the color oxide stripped from the non-printing areas which are then etched in an iron perchloride solution, as above described.

In either case, the iron perchloride will produce on the stainless steel a dull gray etched surface which is substantially the same color as that of etched zinc but which is very susceptible to oxidation or rusting particularly in the case of low-chrome alloy steels. In order to repassivate this surface and convert it to its original whiteness it may be subjected to an electrolytic treatment as anode in an electrolyte comprising the ingredients set forth in the above formula used for coloring the steel. The electrolyte should be used at normal atmospheric temperatures and the plate treated for about 1 minute with a current density of about 1 ampere per sq. in. of surface considering one side only of the anode.

While I prefer in the manufacture of deep-etched or relief plates to use iron perchloride as an etching medium and thereafter to passify the etched surfaces by an electrolytic treatment as above described, it is to be understood that other etching media which do not injure the resist or tend to creep under the edges thereof may be employed. For example, the etching may be done electrolytically by treating the surface as anode in an electrolyte containing the same ingredients and in the same proportions as is recommended for coloring the steel. Such treatment at a current density of from 1 to 2 amperes per sq. in. of surface to be etched will simultaneously etch and passify the steel. For such etching, however, I prefer to use an electrolyte formed by mixing—

	Parts by weight
Water	900
Sulphuric aid (1.84 sp. gr)	330
Sodium dichromate	180

From the foregoing it will be apparent that my plate, except in those cases where the albumen image is permitted to remain on the plate until worn off, is substantially an integral structure consisting entirely of metal and metal oxides, and therefore has wear resisting properties far superior to metal plates upon which the printing image consists only of an adhering film of albumen, gelatine or asphalt. Where such plates are used for printing directly upon metal or other particularly hard surfaces as in the case of tin plate, etc. their resistance to wear is especially advantageous. In addition, it will be found that much finer details may be accurately produced than is possible with any of the present types of albumen or gelatine coated plates.

What I claim is:

1. A printing plate formed of alloy steel containing at least 6%, by weight, of chromium and having printing and non-printing areas thereon, said printing areas comprising a colored film substantially integral with said steel containing oxides of iron and chromium and forming the printing image; the non-printing areas of said plate being substantially free of said oxide film.

2. A photo-lithographic printing plate formed of chromium-containing alloy steel and having a photographic printing image substantially integral therewith comprising oxides of the metals in said steel, and non-printing areas on said plate substantially free of said oxides.

3. A photo-lithographic printing plate formed of chromium-containing alloy steel and having printing and non-printing areas thereon; said printing areas being in relief and comprising an ink-sensitive film substantially integral with said plate containing oxides of the metals in said steel and forming the printing image; said non-printing areas being substantially free of said oxide film.

4. A deep-etched photo-lithographic printing plate formed of a chromium-containing alloy steel having printing and non-printing areas thereon; said non-printing areas comprising a film containing oxides of the metals in said steel and being substantially integral with said plate, and said printing areas being substantially free of said oxide film.

5. Those steps in the method of making a photo-lithographic printing plate having a metallic, ink-sensitive, printing image thereon which comprise applying a light sensitive film to the surface of a chromium-containing alloy steel plate having an ink-sensitive film substantially integral with said surface formed of oxide of the metals in said alloy, imparting the image to said light sensitive film, developing said plate, applying a resist to said image, and thereafter stripping said oxide film from the exposed portions of said plate.

6. Those steps in the method of making a photo-lithographic printing plate having a metal-

lic, ink-sensitive, printing image thereon which comprise applying a light sensitive film to the surface of a chromium-containing alloy steel plate having an ink-sensitive film substantially integral with said surface formed of oxide of the metals in said alloy, imparting the image to said light sensitive film, developing said plate, applying a resist to said image, and thereafter subjecting said plate to electrolytic treatment to strip said oxide film from the exposed portions of said plate.

7. A photo-lithographic printing plate formed of alloy steel containing chromium in a quantity at least sufficient to render said plate highly resistant to corrosion, and having an ink-sensitive printing image thereon comprising oxides of iron and chromium substantially integral with said plate; the other portions of said plate being free of said oxides.

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