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PLANOGRAPHIC PRINTING PLATE AND METHOD FOR PREPARING SAME

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This invention relates to a planographic printing plate and to a method for making such a plate. More particularly, it relates to a method for preparing a sealed hydrophilic layer or layers on a planographic printing plate and to the plate resulting therefrom.

In the following specification and claims it will be understood all parts and percentages are by weight unless otherwise indicated.

The art of planographic printing depends upon the immiscibility of grease and water and upon the preferential retention of a greasy image-forming substance by the image areas, and a similar retention of an aqueous dampening fluid by non-image areas. When a greasy image is imprinted on a suitable surface, and the entire surface is then moistened with an aqueous solution, the image areas will repel the water, and the non-image areas will retain the water. Upon subsequent application of greasy ink, the image portions retain the ink, whereas the moist, non-image areas repel it. The image is then transferred to paper or cloth, via an intermediate, so called off-set cylinder, which is necessary to prevent mirror image printing.

A planographic printing plate is prepared by coating a suitable substrate with a photosensitive emulsion, either by the manufacturer or by the lithographer, and subsequently exposing the thus sensitized plate to actinic light through a photographic image. The exposed plate is thereafter treated to produce oleophilic ink-receptive image portions and hydrophilic ink-repulsive non-image portions, which may be utilized to produce plural copies.

Depending upon the nature of the photosensitive emulsion employed, the treated plate may be utilized to directly reproduce the image to which it is exposed, in which case it is termed a positive-acting plate, or to produce an image complementary to that to which it is exposed, in which case it is termed a negative-acting plate. In either case the image areas of the photosensitive emulsion are rendered oleophilic by appropriate treatment and the remaining portion of the emulsion is removed by a desensitizing treatment to define the hydrophilic non-image areas.

It has been known to use, as the base material for photolithographic plates, either a waterproof paper or a flexible sheet of metal. Typical metals which may be used are aluminum, steel, zinc, magnesium, chromium and copper.

Because paper is relatively coarse grained and has a tendency to stretch, a plate having a metallic base provides finer reproduction and longer service than does a paper base plate. In coating a metallic plate with a light-sensitive material, however, it is necessary to initially provide the metal with a hydrophilic surface to which the light-sensitive emulsion adheres, which defines the ink-repulsive non-image areas upon removal of portions of the exposed light-sensitive material. It is known to produce such hydrophilic surfaces on metallic plates for planographic printing purposes by various procedures. One such procedure is disclosed in copending application Serial No. 44,843, filed on July 25, 1960, now abandoned, and involves treatment of a metallic surface with a titanium hexahalide to provide a hydrophilic layer thereon, followed by sealing such layer in a hot water bath. This procedure and others heretofore known have not been

entirely satisfactory in that the printing plates produced thereby often have limited shelf lives and limited water-receptivity. Moreover such plates tend to absorb moisture and are unsuitable in moist, warm atmospheres, thereby creating packaging and storage problems under such conditions.

It is accordingly among the objects of the present invention to provide a method for preparing a planographic printing plate having a hydrophilic layer thereon, which plate is stable under relatively high humidity and temperature conditions.

A further object of the invention is to provide such a method and the resulting printing plate, which is simply and economically produced and which may be utilized for relatively long press runs.

These and other objects of the invention will be more clearly understood from the following description thereof.

In accordance with the present invention, a method is provided for preparing a planographic printing plate which involves treating a metallic surface with a transition metal fluoride, viz., an acid, alkali metal, or alkaline earth metal salt of the transition metal tetrafluorides, pentafluorides or hexafluorides, to form a hydrophilic layer on the metallic surface, sealing such layer with chromic acid and thereafter applying a photosensitive emulsion in superposed relation over the resulting sealed hydrophilic layer. The thus sensitized printing plate is exposed to actinic light defining a photographic image and the exposed plate is treated to produce an adhering oleophilic image thereon which may be utilized to produce plural copies.

Surprisingly, the chromic acid sealed hydrophilic layers thus formed are markedly stable under high humidity and temperature conditions, and the resulting plates may therefore be stored for long periods of time under such conditions. Printing plates having hydrophilic layers sealed by hot water treatments, on the other hand, absorb moisture and break down when exposed to 90% relative humidity for periods of from one to two days, whereas printing plates having hydrophilic layers sealed by chromic acid in accordance with the present invention, retain their stability for periods upwards of six months, even when stored in moist, warm atmospheres.

The novel hydrophilic surface formed in accordance with the treatment of the invention may be applied to metallic surfaces of various types. Preferably, aluminum plates are utilized in which the aluminum base is chemically etched, mechanically grained or degreased, as desired. Nevertheless, while the treatment of aluminum plates is specifically described hereinafter, it will be understood that the invention may be utilized in connection with any of the well known metallic substrates for printing plates.

The hydrophilic layer is formed on the metallic base by immersing the base in an aqueous solution of an appropriate transition metal tetra-, penta-, or hexafluoride. Any of the group IVB (zirconium, titanium or hafnium) metal salts may thus be employed. Illustrative transition metal fluorides useful in the practice of the invention include zirconium tetrafluoride (ZrF_4), hydrofluozirconic acid (H_2ZrF_6), potassium zirconium hexafluoride

(K_2ZrF_6)

sodium zirconium hexafluoride (Na_2ZrF_6), potassium zirconium pentafluoride ($KZrF_5$), sodium zirconium pentafluoride ($NaZrF_5$), titanium tetrafluoride (TiF_4), potassium titanium hexafluoride (K_2TiF_6), hafnium tetrafluoride (HfF_4), potassium hafnium hexafluoride (K_2HfF_6) and sodium hafnium hexafluoride ($NaHfF_6$). In addition to the acids and alkali metal salts indicated above the alkaline earth metal salts and ammonium salts of

the transition metal fluorides, e.g., $CaZrF_6$ and

$(NH_4)_2ZrF_6$

may be utilized to form the hydrophilic layer, although treatment with the latter salts tends to produce plates having more limited shelf life.

The transition metal fluorides which may be utilized in accordance with the present invention thus include titanium tetrafluoride (TiF_4), zirconium tetrafluoride (ZrF_4), hafnium tetrafluoride (HfF_4) and pentafluorides and hexafluorides having the formula $M_1M_2F_n$, in which M_1 may be either hydrogen, alkali metal, alkaline earth metal or ammonium radicals, M_2 may be either a titanium, zirconium or hafnium cation, and n is either 5 or 6.

It is preferred to immerse the metallic base in an aqueous solution containing from about 0.01% to 1% of the transition metal fluoride. The temperature of the fluoride treating bath is maintained within the range of from about 70° to 180° F., the pH of the solution being regulated within the range of from about 3.5 to 5. The time of immersion is not critical and preferably is varied from as little as five seconds to as much as five minutes. It will be understood that, within the ranges indicated above, the temperature, time and concentration of the transition metal fluoride may be varied to produce optimum results. If desired, a soluble zinc salt may also be included in the transition metal fluoride solution in the manner described in application Serial No. 29,133, filed May 16, 1960, now abandoned.

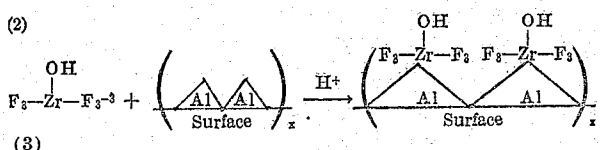
The hydrophilic layer thus produced is sealed by treatment with chromic acid which material may, if desired, be incorporated in the transition metal fluoride treating bath in an amount of from about 0.001% to 2.5% but as indicated hereinafter is preferably incorporated in a separate treatment bath subsequent to formation of the hydrophilic layer. The separate aqueous chromic acid treatment bath contains from about 0.001% to 2.5%, preferably about 0.02%, Cr_3 and is maintained at a temperature of from about 70° F. to 180° F., preferably at about 160° F. The metallic base having the hydrophilic layer thereon is immersed in the chromic acid sealing bath for a period which may vary from about one minute to nine minutes, preferably lasting about three minutes.

The chromic acid treatment seals the hydrophilic layer, thereby minimizing moisture absorption and producing the improved temperature and humidity stability characteristics described hereinabove. The exact mechanism by which the transition metal fluoride and chromic acid react to produce a sealed hydrophilic layer on the aluminum or other metallic substrate is not known. It is possible that the chromic acid forms a chromate layer atop a hydrophilic fluoride layer formed on the metallic substrate, sealing the pores in the fluoride coating. Alternatively, the transition metal fluoride may be bound directly to the metallic plate and cross-linked by the dehydrating action of chromic acid according to the following equations illustrating the possible reaction mechanism when hydrofluozirconic acid is utilized to form the hydrophilic layer:

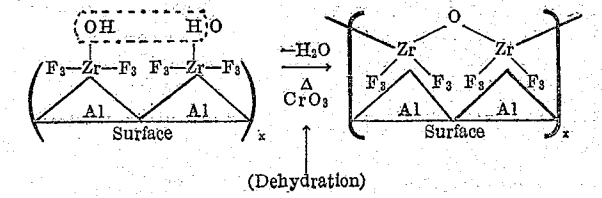
(1)

$$H_2ZrF_6 \xrightarrow{H_2O} F_3{-}Zr(OH){-}F_3^{-3} + 3H^+$$

(2)



(3)



It will be understood that the above reaction mechanisms provide possible explanations of the operation of the invention but are not intended to be limiting thereof.

The photosensitive emulsion coated on the printing plate comprises any of the commonly available light-sensitive materials useful for lithographic purposes, such as the light-sensitive diazo resins, bichromated albumin, gum, casein, furfural-acetone condensation products or cinnamyl resinous materials, utilized alone or in combination. It is preferred, however, to utilize a light-sensitive diazo resin coating as the photosensitive emulsion applied atop the chromic acid sealed hydrophilic layer. It has unexpectedly been found that such a coating is more strongly bonded to such layer than to previously known hydrophilic layers. Diazo sensitized printing plates prepared according to the invention have thus provided extremely long press runs, upwards of 10,000 copies being produced without difficulty.

Any of the well known light-sensitive diazo materials, such as those disclosed in column 5 of U.S. Patent No. 2,937,085, in column 2 of U.S. Patent No. 2,649,373 or referred to in column 10 of U.S. Patent No. 2,714,-066, may be utilized. Any of these or other conventional diazo sensitizers, which are negative-acting, may be treated in the manner disclosed in copending application Serial No. 126,502, filed on July 25, 1961, now U.S. Patent No. 3,113,023, if desired, to provide a positive-acting plate.

A typical light-sensitive diazo resin useful in the practice of the present invention is the condensation product of paraformaldehyde and paradiazodiphenylamine. Employing this resin, the diazo coating may comprise, for example, 1% of the resin dispersed in a saponin solution.

The thus sensitized plate is thereafter exposed imagewise to actinic light to form a permanent oleophilic image. The latent image produced by exposure is developed by means of a suitable lacquer or other developer, producing an oleophilic image and leaving hydrophilic non-image portions exposed on the underlying hydrophilic layer. The plate can then be placed on a press and a large number of copies made therefrom.

It is preferred that, prior to treatment with the transition metal fluoride, the surface of the metallic base, e.g., aluminum, be degreased and chemically activated in order that a more strongly adhering image can be obtained. Consequently, the aluminum is preferably subjected to pretreatment with an alkali degreasing agent, an acid etch, a desmutting reagent, and with a further acid reagent containing an acid such as phosphoric acid, chromic acid, nitric acid, sulphuric acid or oxalic acid, which activates the aluminum surface and increases its receptivity for the subsequent formation of the hydrophilic layer thereon.

Typical acid etching treatments known in the art, such as those described in U.S. Patent No. 2,882,153, may be employed. If a grained plate is desired the aluminum base is not etched but is rather grained by suitable mechanical means, e.g., by rubbing with an abrasive, sandblasting or brushing with a wire, nylon or hair brush. Details of such mechanical graining procedures are found in the prior art, e.g., see U.S. Patent No. 2,882,155.

It is preferred to employ either phosphoric or oxalic acid in the acid activating bath in a concentration in the range of from about 0.01% to 5% by weight, optimum results being obtained when employing such acids in concentration ranges of from about 0.2% to 1%. The time of immersion in the acid bath, which is maintained at between about 50° F. and 100° F., preferably at about 65° F., is varied between about one second and three minutes, with five to ten seconds giving good results, depending on the concentration of the bath. The time, temperature and concentration of such bath may be chosen as desired within the indicated limits to produce optimum results.

The following examples are given for illustrative purposes; it will be understood that the invention is not limited to these examples.

Example I

A sheet of 3S aluminum (99% purity) was degreased and etched in a 10% solution of trisodium phosphate at 160° F. for a period of three minutes. The plate was thereafter rinsed in tap water for three minutes at room temperature and then immersed in a desmut solution for 10 to 15 seconds, the solution containing 15% sulphuric acid and 2.6% chromic acid. The plate was then removed and rinsed in running tap water for three minutes at room temperature.

The pre-treated plate was immersed in a 0.18% solution (pH=4) of potassium zirconium hexafluoride for three minutes. The solution was maintained at a temperature of from 150° F. to 160° F. during the immersion. Immediately after removal from the hexafluoride treating solution the plate was immersed in a chromic acid bath containing .03% CrO_3, which bath was at 150° F. to 160° F. After three minutes in the latter bath, the plate was removed, rinsed with water, dried and sensitized by applying a solution of a diazo resin to both sides of the aluminum sheet. The diazo resin employed was the condensation product of paraformaldehyde and paradiazodiphenylamine (containing four parts of formaldehyde per thirty parts of paradiazodiphenylamine). The coated plate retained approximately 0.25 cc. of the diazo resin coating solution per side and, after drying, was ready for use.

Upon exposure to a source of ultra-violet light through a negative, a strong, water-insoluble image was formed on the surface of the plate. After redeveloping the image five times, the plate was placed on a printing press and over 10,000 sharp and clear copies run.

Example II

Upon following the procedure described in Example I, substituting titanium tetrafluoride for the potassium zirconium hexafluoride employed to form the hydrophilic layer on the aluminum surface, similar results were obtained, and clear distinct copies were formed upon printing with the resulting planographic printing plate.

Example III

An aluminum plate was degreased, etched and rinsed in the manner described in Example I. The plate was then immersed in a desmut solution containing 6% sulphuric acid and 1% chromic acid.

After rinsing the pre-treated plate it was immersed in a 0.06% solution of hydrofluozirconic acid at 70° to 90° F. for three minutes. The hydrophilic layer thus formed was thereafter sealed by immersing the treated plate in a bath containing a mixture of 0.03% chromic acid and 0.007% hydrofluozirconic acid.

The thus sealed hydrophilic layer was coated with the light-sensitive diazo resin coating, exposed and treated in the manner described in Example I above. The resulting printing plate produced clear, sharp copies upon printing.

The present invention thereby provides a method for preparing planographic printing plates, and the resulting plates, which are stable under relatively high humidity and temperature conditions and which provide long press runs. Since various changes may be made in carrying out the above method and in the structure of the resulting printing plate without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A method for preparing a pre-sensitized planographic printing plate comprising, treating an aluminum surface with an aqueous solution containing from 0.01% to 1% of a transition metal fluoride selected from the group consisting of TiF_4, ZrF_4, HfF_4, and a compound having the formula $M_1M_2F_n$, in which M_1 is a cation selected from the group consisting of hydrogen, an alkali metal, an alkaline earth metal and ammonium, M_2 is selected from the group consisting of Ti, Zr and Hf, and n is an integer from 5 to 6, at temperatures between 70° F. and 180° F., to form a hydrophilic layer thereon; subsequently sealing said layer by reacting the same with a solution containing from 0.001% to 2.5% chromic acid at temperatures between 70° F. and 180° F.; and applying a light-sensitive diazo resin coating over the resulting sealed hydrophilic layer.

2. The method for preparing a pre-sensitized planographic printing plate as defined in claim 1, including the further step of exposing the thus treated plate to actinic light and treating the exposed plate to produce an adhering oleophilic image thereon.

3. The method defined in claim 1, in which said transition metal fluoride is a zirconium hexafluoride.

4. The method defined in claim 1, in which said transition metal fluoride is zirconium tetrafluoride.

5. A presensitized planographic printing plate, produced by the method defined in claim 1.

6. The presensitized planographic printing plate as defined in claim 5, in which said transition metal fluoride is a zirconium hexafluoride.

7. The presensitized planographic printing plate as defined in claim 5, in which said transition metal fluoride is zirconium tetrafluoride.

8. A method for preparing a presensitized planographic printing plate comprising forming a hydrophilic layer on at least one surface of a degreased aluminum sheet by treating the same with a solution of from 0.01% to 1% of a transition metal fluoride selected from the group consisting of TiF_4, ZrF_4, HfF_4, and a compound having the formula $M_1M_2F_n$, in which M_1 is a cation selected from the group consisting of hydrogen, an alkali metal, an alkaline earth metal and ammonium, M_2 is selected from the group consisting of Ti, Zr and Hf, and n is an integer of from 5 to 6, said solution being maintained at a pH between 3.5 and 5 and at a temperature between 70° F. and 180° F., for a period of from five seconds to five minutes, subsequently sealing said hydrophilic layer by treatment with a solution of from 0.001% to 2.5% chromic acid at a temperature between 70° F. and 180° F. for a period of from one to nine minutes, and thereafter applying a light sensitive diazo resin coating over said hydrophilic layer.

9. The method defined in claim 8, in which said transition metal fluoride is a zirconium hexafluoride.

10. The method of claim 8 in which said transition metal fluoride is zirconium tetrafluoride.

11. A method of making an aluminum base planographic printing plate comprising treating a degreased aluminum sheet with an aqueous solution of from 0.01% to 1% potassium zirconium hexafluoride at a temperature between 70° F. and 180° F. to form a hydrophilic surface thereon, subsequently sealing said hydrophilic surface by treating the plate with a chromic acid bath containing from 0.001% to 2.5% CrO_3 at a temperature between 70° F. and 180° F., applying a light-sensitive diazo resin coating over the resulting sealed hydrophilic layer, said diazo resin comprising the condensation product of paraformaldehyde and paradiazodiphenylamine, exposing the thus sensitized plate to actinic light and treating the exposed plate to produce an adhering oleophilic image thereon.

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