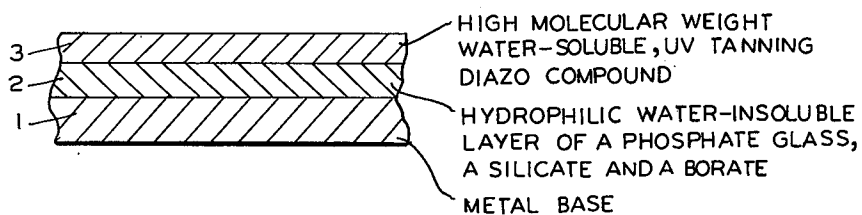


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TREATMENT OF METAL SURFACES FOR THE MANUFACTURE
OF LITHOGRAPHIC PLATES
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3,030,210

TREATMENT OF METAL SURFACES FOR THE MANUFACTURE OF LITHOGRAPHIC PLATES**Paul Chebiniak, Binghamton, N.Y., assignor to General Aniline & Film Corporation, New York, N.Y., a corporation of Delaware****Filed Feb. 12, 1959, Ser. No. 792,820****9 Claims. (Cl. 96—75)**

The present invention relates to the treatment of metal surfaces to provide thereon a hydrophilic layer capable of being light sensitized to produce lithographic plates and to plates containing such surface-treated metal bases. More particularly, the invention is concerned with the surface treatment of aluminum containing metal bases for lithographic purposes.

The use of aluminum and aluminum alloy plates for planographic printing purposes is well known in the art. It is also known that aluminum is a very active element and readily combines with the oxygen of the air to form oxide films of unknown composition. In recent years, a great deal of effort has been directed towards treating aluminum with solutions containing materials serving to passivate the surface of the metal to render it resistant to corrosion.

One of the earliest methods of passivating the aluminum surface was by "anodizing." In this process, a superficial film of aluminum oxide is formed on the surface of the aluminum when it has been made the anode of an electrolytic cell. The first successful anodizing process was introduced in 1924 (British Patent 223,994, U.S. Patent 1,771,910). Since then, many other modifications have been developed. The oxide films formed have been found by X-ray and electron diffraction methods to be amorphous Al_2O_3 . Sometimes the film formed is further modified by "sealing" in hot water. This treatment converts the oxide into a monohydrate of somewhat greater volume.

In recent years protective coatings which are neither metallic nor of the paint type have come into prominence. They provide an insulating barrier of exceedingly low solubility between the metal and its environment through the conversion of the metal surface into a corrosion-resistant, non-reactive form. Such coatings are known as chemical conversion coatings and they are generally highly absorbent. One process by which such films are formed is known as "phosphating" and involves treating the aluminum with a solution of phosphoric acid containing other elements acting as accelerators. In this process crystalline salts of the metal being treated or of metal ions added to the phosphating solution form a coating on the aluminum.

Chromate conversion coatings were highly popular during World War II. The bath compositions for this process contain two basic ingredients: hexavalent chromium as chromate ions and a mineral acid. (See U.S. Patent 2,035,380.) The film formed in this bath has been found to be a basic chromate of the general formula $Cr_2O_3 \cdot CrO_3 \cdot xH_2O$.

Many other types of converting baths are commercially available. Some of these are described in U.S. Patents 2,475,946, 2,568,936, 2,796,371 and 2,820,731. All of them seek to modify the surface to form non-metallic oxide films and impart corrosion resistance to the aluminum.

Before aluminum can be successfully used for planographic printing plates, certain inherent disadvantages of this metal must be overcome. For example, the surface of the aluminum must be treated in some manner so as to provide a passive film on the surface of the aluminum to prevent the corrosion products of the aluminum from forming scum spots on the plate during a press run. In

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addition, the film deposited has to be such that the image will firmly adhere to the aluminum base material, and the non-image areas of the plate have to be hydrophilic and free from any tendency to scum during a press run.

At first, anodized aluminum was used to provide such a surface film. Examples of such plates are familiar to those skilled in the art. Anodized aluminum is, however, relatively expensive to manufacture and with the advent of the presensitized plates, wherein the plate is not reused, it became impractical to employ this process.

Many chemical conversion baths have been used in attempts to apply a suitable film on the aluminum for lithographic purposes and in this connection, reference is made to U.S. Patent 2,507,956. This process is quite satisfactory for users of plates made by the albumin-bichromate process. However, it is quite unsatisfactory for presensitized plates because the nature of the film deposited is such that upon storage the quality of the plate deteriorates, as evidenced by the multiplicity of areas on the plate which become hydrophobic and ink receptive.

A successful chemical treatment for aluminum is described in U.S. Patent 2,714,066. By the process of this patent, it was possible to produce a film on the surface of aluminum with desirable lithographic properties, i.e., the image adhered well to the plate and the non-image areas of the plate were water receptive and were capable of running cleanly on the press. The presensitized plates described in said patent can be further modified as described in British Patent 764,442.

Although the plate described in U.S. Patent 2,714,066 is a commercial item, it has certain limitations, to wit: (1) the image is not visible on the plate immediately after exposure, (2) the plate has a limited storage life, especially under conditions of heat and humidity, and (3) the press life of the plate is sometimes variable, especially if the image is not covered with a coating of lacquer before being run on the press. It would be desirable to increase the number of reproductions from such a plate over that currently possible. Room, therefore, exists for improvements in treating an aluminum or other metal surface for the manufacture of lithographic plates.

It is, therefore, an object of this invention to produce a negative-working, presensitized, aluminum lithographic plate by relatively uncomplicated means through deposition of a transparent, glassy film on the surface of a sheet of aluminum.

It is a further object to produce a presensitized metal plate having good light sensitivity and capable of being stored for long periods of time, especially under conditions of high heat and humidity, without visibly affecting the quality of the plate or length of run.

It is a still further object to produce a sensitized plate in which the light-struck image is tenaciously bonded to the base metal and in which the non-image area will be clean running.

It is also an object of this invention to produce sensitized plates on which the image will be clearly visible immediately upon exposure without resorting to hand inking or lacquering operations.

It is a further object of this invention to produce sensitized lithographic plates made from either grained or ungrained aluminum.

I have found that by treating a piece of aluminum or other metal used in lithography in a hot aqueous solution of a water-soluble phosphate glass, a water-soluble silicate and a water-soluble borate, a layer having excellent lithographic properties is deposited upon the surface of the metal. For instance, when a piece of aluminum is treated with such a solution, dried, and subsequently sensitized with an aqueous solution of a diazo compound of high molecular weight which tans under exposure to U.V.

light, and then exposed under a negative to actinic light and developed in an acid-gum solution such as is commonly employed in lithography, a positive image results which has good ink receptivity, is firmly bonded to the metal base material and has good durability when run on an offset press or duplicator. In addition, this plate can be subjected to extreme conditions of heat and humidity without any perceptible degradation of the quality of the image.

The invention is further illustrated in the accompanying self-explanatory drawing which discloses in section the raw plate compounded as indicated.

Reference numeral 1 on the drawing indicates the metal foil base which is preferably aluminum but which may be an aluminum alloy or another metal useful in forming lithographic plates, such as copper, lead or zinc. The metal base 1 is overcoated with the hydrophilic layer 2 composed of a uniform admixture of phosphate glass, a silicate and a borate. The hydrophilic layer 2 is in turn overcoated with the sensitized layer 3 in which the sensitizer is a high molecular weight, water-soluble diazo compound which is tanned by U.V. light.

As is evident from what has been said, the gist of my invention involves the formation of the hydrophilic layer 2 to which the sensitized layer 3 is applied. This layer 2, which is continuous, transparent, water-insoluble, hydrophilic and resistant to dilute acids, to abrasion and to air oxidation, is formed by coating on metal base 1 an aqueous solution of the following essential components and then drying the coating:

(1) An alkali metal or alkaline earth metal phosphate glass in a concentration sufficient to deposit a thin phosphate glass film on the metal base, i.e., from 2 to 15% by weight;

(2) An alkali metal silicate in an amount of from about 0.5 to 3% by weight; and

(3) An alkali metal or alkaline earth metal borate, phosphomolybdate or silicomolybdate in an amount of 0.5 to 3% by weight.

Preferably, the phosphate glass employed is a sodium phosphate glass, i.e., a true glass which may be thought of as a transparent polymeric sheet. The composition of sodium phosphate glasses extends from a mol ratio of $\text{Na}_2\text{O}:\text{P}_2\text{O}_5$ of 1:1 to 1.7:1 although most sodium phosphate glasses contain a mol ratio of $\text{Na}_2\text{O}:\text{P}_2\text{O}_5$ of between 1:1 and 1.34:1. These glasses maintain a high degree of molecular identity when dissolved in water. Glasses having a composition of greater than



tend to be crystalline. Nevertheless, all sodium phosphate glasses having a molecular composition of



from 1:1 to 1.7:1 have been found to be suitable for my purposes.

However, I am not limited to the use of the sodium phosphate glasses since phosphate glasses containing an alkali metal cation other than sodium, i.e., potassium or lithium or an alkaline earth metal cation such as calcium, barium or strontium, may likewise be employed. The only prerequisites that the phosphate glass must satisfy are that it be a true glass in the sense of the sodium phosphate glass and that it be sufficiently soluble in hot water to provide an effective concentration for laying down the hydrophilic film. Phosphate glasses having a cation of the alkali and alkaline earth metals and suitable for my use are described in J.A.C.S., volume 72, page 661.

The preferred second component of the composition is sodium metasilicate which contains a mol-to-mol ratio of Na_2O to SiO_2 . Other silicates having other ratios of soda to silicate or having an alkali metal cation other than sodium, i.e., lithium or potassium, may also be employed. It is readily apparent to those skilled in the art that such

silicates of alkali metals which have sufficient solubility in hot aqueous solutions will function satisfactorily.

The third essential component is an alkali metal or alkaline earth metal borate, silicomolybdate or phosphomolybdate complex. Thus, there may be employed borax, potassium tetraborate, sodium or potassium metaborate, lithium tetraborate, lithium metaborate, calcium metaborate, strontium metaborate, sodium silico-12-molybdate, sodium-2-phospho-18-molybdate, sodium phospho-12-molybdate or the like. Other hetero polymolybdates which are soluble in water and which are known compounds may also be effectively employed.

The bath compounded as stated is used at temperatures of 95° C. although temperatures ranging from 50 to 100° C. under normal atmospheric conditions will function to produce the desired effect. Preferably, a clean sheet of aluminum, aluminum alloy or other metal is treated in the designated bath for a period of three minutes although longer and shorter periods of time produce operable plates. However, no new effects are gained by immersion times over three minutes.

When a sheet of aluminum or other metal is treated as described, washed and dried, it becomes uniformly coated with a thin, water-insoluble, hydrophilic phosphate glass layer. Such layer is readily amenable to sensitization with a water-soluble, high molecular weight, light-sensitive diazo compound such as tan under U.V. light. Diazo compounds meeting these prerequisites are described, for instance, in U.S. Patents 2,714,066, 2,773,779 and application Serial No. 779,489, filed on December 10, 1958, by Clifford E. Herrick, Jr., and the applicant entitled "Negative Working Offset Plates."

Examples of such sensitizers are:

- 35 The condensation product of p-anilinobenzenediazonium sulfate and formaldehyde
- p,p'-Iminodibenzenediazonium chloride
- N-methyl-p-anilinobenzenediazonium chloride
- 2,5-diethoxy-4-lauramidobenzenediazonium chloride
- 40 N,N' - trimethylenebis(p - ethylaminobenzenediazonium chloride)
- p,p'-Iminodibenzenediazonium chloride reacted with formaldehyde
- N-benzyl-N-ethyl-p-aminobenzenediazonium chloride
- 45 N - (2,6 - Dichlorobenzyl) - N - ethyl - p - aminobenzenediazonium chloride
- 2,5 - diethoxy - 4 - (p - ethoxyphenoxy) benzenediazonium chloride
- 4-(p-Bromoanilino)-2,5-dibromobenzenediazonium chloride
- 50 p-(2,4,6-trichloroanilino)benzenediazonium chloride
- 4 - anilino - 3 - (2,5 - diethoxyphenylsulfamoyl) benzenediazonium chloride
- 2,5-dipropoxy-4-(p-tolylthio)benzenediazonium chloride

55 The diazo compounds used as sensitizers should, in general, possess the following characteristics:

(1) They contain light-sensitive groups contributing primarily to water solubility, e.g., a diazonium group(s).

(2) The light-sensitive molecule is fairly large, mainly containing at least two groups of the size of phenyl or substituted phenyl groups.

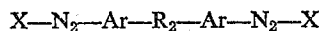
(3) The molecular fragment left when the light-sensitive group imparting water solubility has left the molecule tends to be reactive especially with molecules similar to itself so that a species of photopolymerization results.

(4) The sensitizers when used in my application thereof yield positive copies from negative originals.

Diazo compounds as a class meeting the aforesaid prerequisites are those of the following formulae:



and



75 wherein R is a phenyl radical such as phenyl, halophenyl,

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i.e., bromophenyl, chlorophenyl or the like, carboxyphenyl, alkylphenyl, i.e., toluyl, ethylphenyl and the like, alkoxyphenyl, i.e., methoxyphenyl, ethoxyphenyl and the like, an aralkyl radical such as benzyl, chlorobenzyl, bromobenzyl and the like, cycloalkyl such as cyclohexyl or acyl, i.e., acetyl, lauroyl, benzoyl and the like; Y is O, S, NH or NR_1 , R_1 being alkyl, i.e., methyl, ethyl, propyl or the like; Ar is an aromatic radical; X is an anion of an acid and R_2 is imino or polyalkylene, i.e., dimethylene, trimethylene or the like. Polymeric diazo compounds which are obtained by reacting the aforesaid diazo compounds with carbonyl compounds such as formaldehyde are preferred.

A plate constituted as stated is exposed to actinic radiation under a negative pattern causing the light-struck areas of the layer 3 to tan and harden with the formation of a positive visible image. The plate is swabbed for a few seconds with water or an acid-gum solution commonly employed for developing lithographic images. The plate is then attached to the plate cylinder of a lithographic offset press whereupon the light-struck image areas will rapidly become inked. Many reproductions can be made from the original plate because the image is strongly bonded to the phosphate glass layer 2 which is strongly bonded to the base material 1 and has little tendency to wear during operation of the press. The non-image areas will reproduce cleanly without any tendency toward scumming because the phosphate glass layer 2 is quite hydrophilic and grease repellent.

It is to be especially emphasized that all three components of my phosphate glass solution must be present to produce said layer 2 on the surface of the metal base 1. If the sodium phosphate glass is used alone, an image can be formed but it is quite friable; if either of the other two components is used singly, no image can be obtained. Combinations of any two of the components can be made to produce a hydrophilic surface but the resulting plates are unsatisfactory for lithographic purposes. The presence of the three components is, therefore, critical and a condition precedent to the attainment of satisfactory results.

I do not understand the exact mechanism by which the three components in solution deposit a layer of glassy material upon the metal surface which is hydrophilic, water-insoluble and resistant to acids and air oxidation and to which the sensitizer tenaciously adheres. However, if the base be aluminum, I believe that the soluble polymeric phosphate glass reacts metathetically with the aluminum base to produce a film of very slightly soluble aluminum phosphate glass upon the surface. The sodium metasilicate appears to act as an inhibitor to prevent etching of the aluminum during the deposition of the glassy layer. The third component seems to act to further insolubilize the film. It is quite possible too that the phosphate ion acts as a chelating agent upon the other two components and makes the film deposited less soluble, less sensitive to acids and more abrasive-resistant. However, regardless of what the exact nature of the mechanism is, suffice it to say that all three components are essential for their synergistic effect to be manifested and to produce a glassy film which is tightly bonded to the base metal and to which the image will adhere tenaciously. It might be added that the film 2 is quite different from those produced by "phosphating" or by any of the chemical conversion coatings since these are quite porous and absorbent in nature and are not particularly hydrophilic upon being dried.

A further aspect of my invention resides in the fact that the plates may either be presensitized by application of the diazo sensitizer before storage or may be sensitized by the consumer by making use of wipe-on sensitizing solutions currently being marketed. Such solutions, for example, are described in U.S. Patent 2,826,501 and the same benefits accrue with such wipe-on solutions as are obtained by presensitization.

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The invention will be further illustrated in the following examples but it is to be understood that the invention is not restricted thereto.

Example I

A 10" x 15" smooth piece of .003" thick aluminum foil consisting essentially of pure aluminum was degreased by solvent degreasing employing acetone. The clean foil was then immersed for three minutes in a bath of the following composition in water:

	Percent by weight
Component I—sodium phosphate glass (ratio of $\text{Na}_2\text{O}:\text{P}_2\text{O}_5$ 1:1 to 1.7:1)-----	5
Component II—sodium metasilicate (mol ratio of silica to soda 1:1)-----	2
Component III—sodium metaborate-----	2

The bath was conveniently maintained at a temperature of 95° C.

Upon removal from the treating bath, the aluminum was washed with cold water and dried. A layer of phosphate glass is now permanently bonded to the aluminum foil. The layer is essentially a continuous transparent film essentially free of water solubility and sensitivity to dilute acids, abrasion-resistant and resistant to air oxidation. The film is permanently hydrophilic and will not become hydrophobic when in contact with heat or the atmosphere.

The plate was next sensitized with a 1% aqueous solution of the zinc chloride double salt of the condensation product of p-anilinobenzenediazonium sulfate and formaldehyde. The aqueous solution may be applied by whirling the plate on a plate whirling machine or automatically by dip-bead air knife technique. The plate is then dried.

The plate may be exposed under a negative pattern to U.V. radiation from a bank of 18-15-watt BL lamps at a distance of approximately 2" in a vacuum light box. Following exposure, the positive image is plainly visible on the plate by virtue of the fact that in the light-struck areas the sensitizer has turned bluish, while in the non-light-struck areas it is a yellow color. The non-light-struck areas of the plate can easily be removed by swabbing the plate for a few seconds with water or an acid-gum solution of the type commonly used in lithography. The light-struck image is thoroughly tanned and is tenaciously bonded to the glass film. It is difficult to abrade or remove the image by rubbing it with a cellulose pad moistened in an acid gum solution. When the plate is attached to the plate cylinder of an office type duplicator, positive copies of the original are obtained. The image on the plate inks rapidly and the non-image areas of the plate have no tendency to scum during the run.

While the aluminum foil employed was specified as having a thickness of .003", other foils having a thickness ranging up to .02" may be used. Furthermore, in lieu of the aluminum foil, use may be made of aluminum alloys or other metallic foils such as copper, lead or zinc.

Instead of cleaning the aluminum foil by use of acetone, any effective degreasing bath may be used such as an acid or alkaline degreasing system, an emulsion system, an electrolytic system or any of the numerous degreasing baths presently available on the market.

Example II

A 10" x 15" sheet of .012" thick aluminum was degreased in an alkaline type degreasing bath, washed, dried, and grained by sandblasting. After treatment in the phosphate glass solution as described in Example I, the plate was sensitized as in Example I, exposed under a negative, developed and attached to the plate cylinder of an offset duplicator, whereupon positive copies were obtained from the negative original. It is of little consequence as to how the grain is applied to the plate. The plate may be grained either by mechanical brushing, sand-blasting, or by chemical means with equally good results.

Example III

Good positive copies were obtained from plates made in essentially the same manner as described in Example I excepting that the sodium metaborate was replaced by 1% of sodium 2-phospho-18-molybdate.

Example IV

Good positive copies were obtained from plates made in essentially the same manner as described in Example I excepting that the sodium metaborate was replaced by 1% of sodium phospho-12-molybdate.

Example V

Good positive copies were obtained from plates made in essentially the same manner as described in Example I excepting that the sodium metaborate was replaced by 1% of sodium silico-12-molybdate.

It is to be understood that the term "hydrophilic" as used herein means that the film 2 is water-receptive but not water-soluble. Similarly, the term "hydrophobic" means that the product so designated is capable of accepting greasy inks and repelling water. The term hydrophobic is, therefore, synonymous with the term oleophilic.

Modifications of the invention will occur to persons skilled in the art. I, therefore, do not intend to be limited in the patent granted except as necessitated by the appended claims.

I claim:

1. A base capable of being sensitized with a water-soluble, high molecular weight diazo compound which tans upon exposure to U.V. light, said base comprising a metal, a surface of which is coated with a continuous, transparent, water-insoluble hydrophilic layer which is resistant to dilute acids, to abrasion and to air oxidation and which is formed by coating the metal base with a hot aqueous solution consisting of about 2 to 15% by weight of a phosphate glass selected from the class consisting of alkali metal and alkaline earth metal phosphate glasses, about .5 to 3% by weight of an alkali metal silicate and about .5 to 3% by weight of a compound selected from the class consisting of alkali metal and alkaline earth borates, -phosphomolybdates and -silicomolybdates, and drying the coating.

2. The article as defined in claim 1 wherein the phosphate glass is a sodium phosphate glass, the silicate is sodium metasilicate and the third component is sodium metaborate.

3. The article as defined in claim 1 wherein the phosphate glass is a sodium phosphate glass containing a

molecular composition of $\text{Na}_2\text{O}:\text{P}_2\text{O}_5$ of from 1:1 to 1.7:1.

4. The article as defined in claim 1 wherein the metal base is aluminum.

5. A lithographic plate comprising a metal base a surface of which bears a continuous, transparent, water-insoluble hydrophilic layer resistant to dilute acids, to abrasion and to air oxidation and which is formed by coating the metal base with a hot aqueous solution consisting of a phosphate glass selected from the class consisting of alkali metal and alkaline earth metal phosphate glasses in an amount of about 2 to 15% by weight, an alkali metal silicate in an amount of from about .5 to 3% by weight and a compound selected from the class consisting of alkali metal and alkaline earth metal borates, -phosphomolybdates and -silicomolybdates in an amount of about .5 to 3% by weight and dried, said hydrophilic layer adhering tenaciously to the surface of the metal base, said hydrophilic layer being overcoated with a water-soluble, high molecular weight, light-sensitive diazo compound capable of being tanned by U.V. light, said sensitizer adhering tenaciously to the hydrophilic surface.

6. The article as defined in claim 5 wherein the phosphate glass is a sodium phosphate glass.

7. The process of producing a hydrophilic layer on a metal surface in the preparation of lithographic printing plates, the improvement which comprises coating a metal surface with a hot aqueous solution of a composition consisting of about 2 to 15% by weight of a phosphate glass selected from the class consisting of alkali metal and alkaline earth metal phosphate glasses, about .5 to 3% by weight of an alkali metal silicate and a compound selected from the class consisting of alkali metal and alkaline earth metal borates, phosphomolybdates and silicomolybdates in an amount of about .5 to 3% by weight, and drying the resulting coating to produce a continuous, transparent, water-insoluble, hydrophilic layer resistant to dilute acids, to abrasion and to air oxidation.

8. The process as defined in claim 7 wherein the coating is effected by immersing the base metal in the aqueous solution at a temperature of from 50-100° C. for a period of a few minutes.

9. The procedure as defined in claim 7 wherein the base metal is aluminum.

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2,714,066	Jewett et al.	July 26, 1955