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LITHOGRAPHIC PLATES, GLUCONATE SOLUTIONS THEREFOR AND PROCESS FOR PRODUCING THE SAME

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10 Claims. (Cl. 96—75)

This application is a continuation of application No. 213,876, filed Aug. 1, 1962, now abandoned.

The present invention relates to lithographic plates, solutions for treating such plates and procedure for producing them, and more particularly, to lithographic plates composed of aluminum, chromium or steel, at least one of the surfaces of which is treated with gluconic acid or a gluconate.

Lithographic plates made of zinc or aluminum in accordance with conventional procedures have a number of recognized disadvantages which make them far from ideal as printing plates. One of the most important disadvantages is that the plates oxidize and the oxided surfaces do not have a definite or uniform chemical character so that the properties of the oxided surfaces continually undego change. This causes a storage problem because such plates, under normal storage conditions, are variable as to their nature. An additional disadvantage of conventional plates is that it is necessary to counteretch them before applying the light-sensitive coating thereto. Where, for example, albumin or like sensitizer remains on non-image areas, scumming occurs because these areas tend to pick up ink during use of the plates, and this is most undesirable because defective prints result in spite of the use of desensitizers for removing undeveloped sensitizer from non-image areas. It has been observed that such plates have a definite tendency to accumulate sensitizer, scumming, or to tone up during use. A further disadvantage of conventional plates is that they are readily subject to corrosion during prolonged periods of storage. This makes it necessary to recondition the plates before they can be used and some plates may be ruined beyond use. Prior known plates other than silicated plates which have been presensitized are very likely to deteriorate during storage so that they are no longer able to be used merely upon exposure to light through a negative or stencil followed by washing away the unexposed light-sensitive material.

When such plates have undergone change or deterioration, they cannot receive and hold adequately the light-sensitive diazo resin or other light-sensitive coating material, nor do they maintain a substantially constant permanency of condition. Such plates, moreover, do not have a long press life and are not free from halation. These and other disadvantages which are understood by those working in the lithographic industry are overcome by the present invention which additionally has advantages peculiar to itself.

According to the present invention, aluminum, chromium or steel plates or sheets are treated with gluconic acid or a gluconate constituting a source of gluconate ions and, subsequently, subjected to sealing operations thereby providing a conversion coating on one or more of the surfaces of the metal sheets. The resulting gluconated sheets or plates combine the desirable physical properties of the untreated sheets with the hereinafter stated and other advantages of a gluconated surface. The products so produced are ideal for lithographic printing plates.

As compared with conventional aluminum and zinc

sheets or plates now used in the lithographic industry, gluconated aluminum, chromium or steel sheets or plates have important advantages and much greater versatility. One such advantage is that a gluconated plate does not undergo oxidation under normal storage conditions and, hence, the chemical properties of the surfaces are substantially constant, thus eliminating deterioration or change due to storage. In contradistinction, ordinary aluminum and zinc sheets do oxidize and continually change with respect to the chemical properties of the surfaces, thereby causing a serious storage problem.

A gluconated sheet or plate has a permanent, durable, hydrophilic surface, and this is extremely important because a printing plate which does not have such a surface in the non-printing areas tends to scum due to the fact that the non-image areas of the printing plate become ink receptive. A gluconated sheet or plate with a hydrophilic image very markedly reduces scumming and, in some cases, eliminates it entierly. A gluconated sheet does not require counteretching prior to the application of the light-sensitive coating, whereas counteretching is accepted standard procedure in processing zinc and aluminum plates of conventional nature. Counteretching necessitates the scrubbing of the sheet with an acid solution to remove loose oil and oxide, neither of which is present on the surface of a gluconated sheet or plate.

A gluconated sheet or plate has the further advantage over known lithographic plates in that all traces of casein, albumin, etc., can be positively removed in the first instance without dependence upon any separate chemical desensitizing processing.

The gluconate treated plate or sheet has the important advantage that it can be used for all three types of lithographic processes, namely, the Deep Etch Process, the Surface Process and the Wipe-On Process. In the Deep Etch Process, a bichromated-gum arabic solution is dried onto the plate surface, exposed through a photographic positive to a light source, developed with an acidic aqueous salt solution to wash away unexposed sensitizer, etched with an acidic ferric chloride solution, optionally plated with electroless copper, and then lacquered and inked. The light hardened stencil is then washed off the plate and the areas of the plate which contained the stencil become the non-printing areas, while those areas which have been developed, etched, copperized, lacquered and inked, are the printing areas. In the Surface Process, a bichromated casein solution is dried onto the plate surface, exposed through a photographic negative to a light source, coated with a layer of lacquer and then with ink and developed with a slightly ammoniacal solution. Those areas of the plate which contained the unexposed, developed (washed away) sensitizer become the non-printing areas, while the light exposed, lacquered and inked areas are the printing areas. In the Wipe-On Process, a diazo resin solution or a solution of a diazo resin combined with a colloid is hand-coated onto the plate surface, following which the plate is exposed through a photographic negative, coated with a layer of ink and developed with an acidic gum arabic solution. Alternatively, the exposed plate can be lacquered and developed in one operation by the use of a lacquer emulsion developer. The unexposed areas of the plate which were developed and washed away become the non-printing areas, while the exposed areas which were lacquered and/or inked become the printing areas.

While in some instances conventional zinc and aluminum plates can be used both in the Deep Etch and Surface Processes, it is necessary to counteretch them first due to their tendency to "scum."

It is well know nthat light-sensitive diazo resins and similar light-sensitive materials are very sensitive to

metals and that is why a conventional zinc or aluminum plate cannot be used for wipe-on platemaking. In contrast, a gluconated plate is ideally suited for use in the Wipe-On Process.

It is also known that a silicated plate can be used for wipe-on platemaking, but is subject to the difficulty that the silicate coating cannot be penetrated by the etches ordinarily used in deep etch platemaking. In contrast, a gluconated plate is admirably suited for deep etch platemaking since it can be etched with the usual deep etch etches.

A lithographic plant can, if such is desired, use and store a single type of lithographic printing plate for all three of the lithographic platemaking processes referred to above by employing a gluconated aluminum, chromium or steel plate according to the present invention.

A gluconated plate can also be presensitized with light-sensitive diazo resins and other similar light-sensitive organic materials and can then be stored for periods as long as several months without any loss of photographic sensitivity.

A gluconated sheet or plate as prepared by the present invention has a still further advantage over prior known sheets or plates in that the treatment with a gluconate can be made directly to the metal sheet while it is being mechanically grained. This provides a great saving in handling costs and equipment because treatment baths can be eliminated. If desired or preferred, however, the gluconate treatment can be carried out in the immersion type of process with an advantage over prior immersion processes in that the gluconate treatment is performed at room temperature.

Plates or sheets treated with gluconic acid or a gluconate in accordance with the present invention can be and have been produced with two different types of surfaces, namely, the so-called "smooth surface" plates produced by chemical etching and "grained" plates produced by mechanical surface treatment. In both instances the surfacing is carried out prior to the treatment with gluconic acid or a gluconate. Theoretically, the smoother the surface of a lithographic plate the greater is the resolution of half-tone dots, but, on the other hand, the greater the surface roughness of the plate the greater is its capacity to receive and hold ink and water. Consequently, there are two types of plates in general use. These are the "smooth surface" plate exemplified by the chemically etched plate, and the "grained" plate exemplified by the mechanically surfaced plate.

The invention is illustrated by the following non-limitative examples.

Example I.—Production of a gluconated sheet with a chemically etched surface

A 10 inch x 15 inch x 0.012 inch sheet of 2S (1100) aluminum was immersed for two minutes at a temperature of 140° F. in a combination cleaner and etch which was prepared by mixing the following ingredients in the order listed and in the proportions set forth:

Water (deionized)	ml	3785
Sodium phosphate (tribasic)	g	28.35
Sodium hydroxide	g	141.75
Sodium lauryl sulfate	g	0.40

The thus treated sheet was rinsed thoroughly with deionized water at room temperature and then immersed in a desmutting bath at room temperature for one minute. The desmutting bath was made up of:

	Ml.
Nitric acid (70%)	1500
Water (deionized)	1500

The slightly grained aluminum was again thoroughly rinsed with deionized water at room temperature and then immersed for two minutes in a gluconate bath at room temperature, the gluconate bath being composed of:

Water (deionized)	ml	3820
Sodium gluconate (99%)	g	140
Nitric acid (70%)	g	40

After again rinsing thoroughly with deionized water at room temperature, the treated aluminum sheet was dried by means of a stream of compressed air.

Example II

The procedure of Example I was followed except that the gluconate bath had the following composition:

Water (deionized)	ml	3640
Gluconic acid (50%)	g	200
Tartaric acid	g	120
Nitric acid (70%)	g	40

The above bath was used at room temperature for two minutes.

Example III

Instead of the gluconate bath of Examples I and II, the following bath was employed:

Water (deionized)	ml	3800
Gluconic acid (50%)	g	200

The above bath was used at room temperature for two minutes and the treated aluminum sheet was rinsed with deionized water at room temperature and then dried over an open gas flame for fifteen seconds. In other respects, the procedure was the same as in Example I.

Example IV.—Production of a gluconate treated sheet with mechanical brush grain

A 26.75 inch x 31 inch x 0.012 inch sheet of 2S (1100) aluminum was degreased by immersing it in a solution of trichloroethylene at room temperature. The sheet was then removed from the solution and allowed to air dry. It was then grained by passing it on an endless belt in a horizontal plane under a set of revolving brass bristle brushes which were located on the perimeter of a rotating circular support. The graining machine employed is described in United States Patent No. 2,948,087. During this operation, the plate was flushed with a slurry of pumice in an aqueous solution, the slurry having the following composition:

#O pumice	g	1600
#F pumice	g	1600
#FF pumice	g	1600
Water (deionized)	ml	4000

	G.
Sodium hydroxide (95%)	4
Sodium gluconate (99%)	20

The plate was allowed to remain in contact with the above slurry for one minute and was then flushed with water to remove the slurry, following which the plate was subjected to treatment with an acid rinse solution composed of four ounces of acetic acid per gallon of water. The acid rinse was permitted to remain in contact with the plate for thirty seconds and the plate was then flushed with tap water to remove the acid rinse completely. The resulting plate was then passed at a distance of six inches over a series of lighted gas burners for forty seconds to dry the plate.

It has further been found that there was a slightly different mechanism involved by using the gluconate on chemically grained, as contrasted with mechanically grained plates. While the reason for this difference is not fully known or understood, the gluconate treatment works over a wide pH range when used in conjunction with an abrasive on the mechanical graining machine, whereas only a strongly acid gluconate treatment solution was found to be best on metal sheets treated by immersion. It

is possible that the difference may be due to the absence of oxide on the metal plate as a result of the mechanical abrasion in the graining machine as oxidation must be contended with in the immersion process. As a result of this difference in mechanism between the two methods of treating metal sheets with gluconate solutions, the treatment solutions themselves differ somewhat in composition as will be apparent from the foregoing examples.

In treating metallic sheets by immersion according to this invention, the optimum concentration of the gluconate ion, irrespective of its source, is 2 to 4 percent by weight of the solution. The optimum pH range is 1.0 to 3.0. These ranges are of critical significance and should not be appreciably departed from. For instance, if the gluconate ion concentration falls appreciably below 2 percent, the treatment time is unduly prolonged, and the entire operation becomes uneconomical. If the gluconate ion concentration rises appreciably above 4 percent, no advantages accrue and the disadvantage arises that closer pH control is required. If the pH value drops appreciably below 1.0, the bath becomes too highly acid and the metal sheet becomes etched. If the pH rises to a value appreciably greater than 3.0, the effectiveness of the gluconate treatment is noticeably decreased.

In the foregoing description of the invention, the source of gluconate ions is either gluconic acid or sodium gluconate. The invention is not, however, limited to these sources of gluconate ions because it has been found that other gluconates can be used without imparting any adverse effects to the system. Other sources of gluconate ions forming a part of the invention are the gluconates of iron, nickel, zinc, calcium, magnesium and potassium. It will be understood, however, as shown in the above examples, that the conditions for optimum use of the gluconate treatment must be somewhat different when the treatment is used in a mechanical graining machine.

Before aqueous gluconate solutions are combined with pumice, such as that of the composition above set forth in Example IV, the pH range of such solutions is between 2.4 and 12.1. The minimum utilizable gluconate ion concentration is 0.5 percent and the maximum is governed by the solubility of the particular source of gluconate ions used, and as a corollary, the overall economics of the entire operation. The gluconate ion concentration must, however, not be permitted to fall below 0.5 percent because in such event, incomplete passivation of the metal plates results.

It has still further been found that there are certain anions which have a beneficial effect on the treatment of the metal plates when such anions are added to the gluconate-pumice mixture. These anions are tartrate, acetate and carbonate ions. In the investigation of this phase of the invention, it was found that phosphate, nitrate and oxalate ions have an adverse effect on the gluconate treatment of the metal plates, and hence, such are to be excluded.

The present invention also includes the discovery that superior gluconate treatment and simultaneously grained metal plates are produced when an alkaline treatment solution is followed by an acidic rinse. The acidic rinse includes aqueous solutions of acetic, formic, gluconic and lactic acids, and all such were found eminently suitable for this purpose. The acidic rinses contained a concentration of one to five ounces of any of the foregoing acids per gallon of deionized water.

From the gluconate treated plates prepared by the procedure of Example I, there have been produced nylon-diazo presensitized plates using a nylon-diazo sensitizer described in United States Patent No. 2,826,501. This nylon-diazo sensitizer, in conjunction with the gluconate treatment, produces a very superior lithographic plate as compared to the use of the same nylon-diazo sensitizer on a silicated aluminum plate. The plate produced by the application of the nylon-diazo sensitizer to the silicated metal surface of the plate is photographically too fast for lithographic purposes, but the same sensitizer on a gluconated plate surface has been found to be ideal for lithographic purposes.

Aluminum plates prepared according to Example IV with a gluconated surface are completely satisfactory for use in the production of deep etch plates, surface plates and wipe-on diazo plates.

The invention can therefore be most satisfactorily used in the treatment of aluminum, chromium and steel plates, at least one surface of which has been gluconated, and all such treated plates are suitable for lithographic printing plates.

The presensitized plates referred to above are prepared by making a chemically grained gluconate treated plate as already described, applying thereto the nlyon-diazo resin solution of United States Patent No. 2,826,501 by wiping the same on by hand or by means of a roller and then air drying the coating thus produced. The presensitized plate is then processed by exposing the coating to a light source through a stencil or negative developing or washing away the unexposed areas with the developer of United States Patent No. 2,826,501, applying a lacquer like that of United States Patents Nos. 2,754,279 or 2,865,873, and rinsing with water.

The nylon-diazo resin solution of Patent No. 2,826,501 is composed of the following constituents in approximately the following amounts, by weight:

	Percent
Water-soluble condensation product of p-diazo diphenylamine and formaldehyde	0.11
Soluble superpolyamide nylon resin	0.94
Non-ionic surface active agent (100%)	0.01
Water	17.15
and	
Denatured ethyl alcohol	76.35
Furfuryl alcohol	5.44

The developer of Patent No. 2,826,501 is composed of the following constituents:

Citric acid	g	1.2
N,N-dimethylformamide	ml	124.5
Furfuryl alcohol	ml	55.2
Methanol	ml	375.0

In a typical application of the deep etch process, a mechanically grained plate produced as in Example IV is centrifugally coated with a bichromated gum arabic solution according to the recommendations of the Lithographic Technical Foundation Publication No. 806. Such solution contains water, gum arabic, ammonium bichromate, a wetting agent (surfactant), a blue dye and ammonium hydroxide. The basic coating solution contains 2840 milliliters of 14° Baumé gum arabic solution, 950 milliliters of ammonium bichromate stock solution (758 grams of photo grade ammonium bichromate in enough water to make one gallon of 14.2° Baumé at 77° F.), and 140 milliliters of ammonium hydroxide (28% NH_3) to which the other ingredients are added. The coating solution has a pH value of 8.8 to 9.0 and tests between 14.0° and 14.2° Baumé at 77° F. Whirling is continued until the coating dries and the coated plate is then exposed to a light source through a suitable positive. The unexposed areas are developed or washed away with an aqueous acidic salt solution of calcium chloride in water to which lactic acid has been added according to the recommendations of Lithographic Technical Foundation Publication No. 806, e.g.:

Zinc chloride (technical)	g	680
Calcium chloride (commercial)	g	1360
Water	ml	1890
Lactic acid (85%)	ml	340

The bared metal is etched in acidic ferric chloride solution according to the recommendations of the above publication, e.g.:

Calcium chloride solution (40–41° Bé.)	ml	2630
Zinc chloride (technical)	g	1000
Iron perchloride solution (50–51° Bé.)	ml	750
Hydrochloric acid (37–38.5%)	ml	37
Cupric chloride	g	70

The plate is next washed with anhydrous alcohol to remove salts and water and a lacquer film applied by hand to the thus treated plate and allowed to dry, following which a developing ink is applied by hand and allowed to dry. The plate is now soaked in warm water which penetrates to the exposed coating leaving the plate with inked image areas. The non-printing areas are hydrophilic due to the previous treatment of the plate.

In a typical application of the Wipe-On Process, using diazo resin solution, a mechanically grained plate produced as in Example IV is wiped on with a pool of diazo resin solution and smoothed down with a soft, non-abrasive applicator and allowed to air dry. The diazo resin solution is a 1 to 5 percent, by weight, aqueous solution of the condensation product of p-diazo diphenylamine and formaldehyde. The plate is next exposed to actinic light rays through a photographic negative and is finished in either of the following ways:

(A) A developing ink of known composition is applied in the same manner as the diazo resin solution and developed with a developer such as one composed of water, gum arabic and phosphoric acid. The developer penetrates through the ink and removes, by dissolving, the unexposed diazo sensitizer coating. The image areas are exposed water-insolubilized diazo resin covered by greasy ink and the non-printing areas are hydrophilic gluconated surfaced.

(B) A lacquer emulsion the same as or similar to that of United States Patent No. 2,865,873 is applied. The image areas are exposed water-insolubilized diazo resin covered by the lacquer composition and the background or non-printing areas are hydrophilic gluconated treated surfaces.

The surface process is carried out according to the recommendations of the Lithographic Technical Foundation Publication No. 807, the contents of which are hereby made a part hereof. The plates are termed "surface plates" and are plates which have been exposed through negatives and on which the exposed coating serves as a base for the ink-receptive image. In general, an aluminum sheet is grained in known manner and cleaned with a counteretch such as acetic acid in water. A light-sensitive coating is applied, with or without (usually without) a prior pre-etch with the same plate etch used for desensitizing. The coating solution is a mixture of a solution of ammonium bichromate and a solution of a colloid such as albumin, casein, gum arabic, gelatin or cellulose gum. The coated plate is exposed to light through a negative to form the image or printing areas. Light passing through the clear portions of the negative hardens or tans the coating under these areas. Any suitable available commercial lacquer is applied to the exposed surface plate and serves as protection for the image areas. A developing ink is then applied to the exposed plate to place a greasy, ink-receptive layer on the image areas and the plate is developed to remove unexposed coating from the non-image areas. The usual finishing operations are then carried out, all as described in the said Publication No. 807.

The term "steel" as used herein means, without limitation thereto, stainless steel and preferably that stainless steel alloy known as 302 stainless steel which is composed of 0.08 to 0.20 percent carbon, 16.0 to 18.0 percent chromium, 6.0 to 8.0 percent nickel, and manganese up to a maximum of 2.0 percent, the balance being substantially all iron.

What is claimed is:

1. A method of preparing a lithographic plate having a permanent, durable, hydrophilic surface which consists essentially in treating an aluminum, chromium or steel plate with an aqueous solution having a pH of 1 to 3 and containing gluconate ions in a 2 to 4% concentration based on the weight of the solution.

2. A method according to claim **1**, in which the gluconate ions are formed in the solution from gluconic acid or a salt of gluconic acid.

3. A method according to claim **1**, in which the plate is chemically etched prior to treating it with gluconate ions.

4. A method of preparing a lithographic plate having a permanent, durable, hydrophilic surface which consists essentially in treating an aluminum, chromium or steel plate with an aqueous gluconate composition containing pumice and which aqueous composition has a gluconate ion concentration not less than 0.5% based on the weight of the composition and a pH of 2.4 to 12.1.

5. A method according to claim **4**, in which one of the anions tartrate, acetate and carbonate is present in the aqueous composition.

6. A method according to claim **4**, in which one of the anions tartrate, acetate and carbonate is present in the aqueous composition and phosphate, nitrate and oxalate ions are absent.

7. A lithographic plate of aluminum, chromium or steel having a permanent, durable, hydrophilic surface gluconated with an aqueous solution having a pH of 1 to 3 and containing gluconate ions in a 2 to 4% concentration based on the weight of the solution.

8. A lithographic plate according to claim **7**, in which the aluminum, chromium or steel is chemically etched before gluconation.

9. A lithographic plate according to claim **7**, in which the chemically etched gluconated plate has thereon and in contact with the gluconated plate a water-soluble diazo resin sensitizer.

10. A lithographic plate of aluminum, chromium or steel having a permanent, durable, hydrophilic surface grained and gluconated due to the action thereon of an aqueous pumice composition containing gluconate ions in a concentration not less than 0.5% based on the weight of the composition and having a pH of 2.4 to 12.1.

References Cited

UNITED STATES PATENTS

2,186,945	1/1940	Wood	101—149.2
3,169,065	2/1965	Sorkin et al.	96—33

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