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[54] **PROCESS OF ELECTROLYICALLY ANODIZING A MECHANICALLY GRAINED ALUMINUM BASE AND ARTICLE MADE THEREBY**

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[63] Continuation of Ser. No. 60,625, Aug. 3, 1970, abandoned, which is a continuation-in-part of Ser. No. 670,403, Sept. 25, 1967, abandoned.

[52] **U.S. Cl.** ..... **204/33;** 96/33; 96/75; 96/86 R; 96/86 P; 101/454; 101/456; 101/459; 101/467; 117/34; 148/6.27; 204/35 N; 204/38 R; 204/39

[51] **Int. Cl.** **C23b 9/02**

[58] **Field of Search** ..... 96/33, 75, 86 R, 86 P; 101/454, 458, 459; 204/33, 35 N, 39.14; 148/6.27; 117/34

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[57] **ABSTRACT**

There is disclosed herein a method of making aluminum supporting base sheets for lithographic plates by graining and subsequently anodizing a surface of the aluminum. The grained and anodized surface has a dark, steel-grey, lusterless appearance, is hard, abrasion resistant and corrosion resistant, and has an exceptional inherent antihalation character.

11 Claims, No Drawings

PROCESS OF ELECTROLYICALLY ANODIZING A MECHANICALLY GRAINED ALUMINUM BASE AND ARTICLE MADE THEREBY

This application is a continuation application of pending application Ser. No. 60,625 filed Aug. 3, 1970, which in turn was a continuation-in-part of my copending application Ser. No. 670,403 filed Sept. 25, 1967 both applications now abandoned.

This invention relates to the preparation of supporting bases for lithographic printing plates, and more particularly to novel anodized aluminum lithographic plate supporting bases having improved abrasion resistance, inherent antihalation characteristics and long press-life.

The art of lithographic printing depends upon the immiscibility of grease and water, upon the preferential retention of a greasy image-forming substance by an image area, and upon the similar retention of an aqueous dampening fluid by a non-image area. When a greasy image is imprinted upon a suitable surface and the entire surface is then moistened with an aqueous solution, the image area will repel the water and the non-image area will retain the water. Upon subsequent application of greasy ink, the image portion retains ink whereas the moistened non-image area repels it. The ink on the image area is then transferred to the surface of a material on which the image is to be reproduced, such as paper, cloth and the like, via an intermediary, a so-called offset or blanket cylinder, which is necessary to prevent mirror-image printing.

The type of lithographic plate to which the present invention is directed has a coating of a light-sensitive substance that is adherent to an aluminum base sheet. If the light-sensitive coating is applied to the base sheet by the manufacturer, the plate is referred to as a "presensitized plate." If the light sensitive substance is applied to the base by the lithographer or trade platemaker, the plate is referred to as a "wipe-on" plate. Depending upon the nature of the photosensitive coating employed, the treated plate may be utilized to reproduce directly the image to which it is exposed, in which case it is termed a positive-acting plate, or to produce an image complementary to the one to which it is exposed, in which case it is termed a negative-acting plate. In either case the image area of the developed plate is oleophilic and the non-image area is hydrophilic.

In the case of a negative plate that is exposed to light through a negative transparency, the light-sensitive material, commonly a diazo compound, is caused to harden and thereby become insoluble in a desensitizing solution which is applied to negative plates after light exposure for the purpose of removing that part of the light-sensitive coating which, because it was protected from the light by the negative, was not light-hardened. The light-hardened surface of a negative plate will be the oleophilic surface which is compatible with the greasy ink and is called the "image area"; the surface from which the non-hardened light-sensitive material has been removed by a desensitizer will be, or can be converted to, a hydrophilic surface having little affinity for the greasy ink and is called the "non-image area."

A positive plate is generally one upon which the non-image area is the portion of the light-sensitive diazo compound exposed to light while the unexposed portion is either oleophilic or adapted to be converted by

chemical reaction to a hardened oleophilic ink-receptive image area.

In coating a metallic plate with a light-sensitive material, however, it is highly desirable initially to provide the metal with a hydrophilic surface to which the light-sensitive coating adheres and which becomes the ink-repulsive non-image area upon removal of the unconverted or unhardened light-sensitive material. It is known to produce such hydrophilic surfaces on metallic plates for planographic printing purposes by various procedures.

Anodizing the surface of the metal base sheet material of a lithographic plate, especially an aluminum sheet, provides certain advantages. Aluminum and other common photographic and lithographic base sheet metals are relatively soft and do not have high resistance to abrasion and corrosion. The oxides of such metals, such as formed on the surface by anodizing, however, in general are harder and more resistant to abrasion, wear and corrosion. Additionally, such oxidized surfaces tend to have as good or better hydrophilic and oleophobic characteristics, both of which are highly desirable in lithographic printing plates, than the unanodized metal surfaces.

Anodized photographic and lithographic plates, particularly aluminum plates, are known and commercially available in the United States and Great Britain. Such plates have been described in various U.S. and foreign patents, including U.S. Pat. No. 2,681,310, U.S. Pat. No. 3,181,461 and U.S. Pat. No. 3,280,734, and British Pat. No. 914,834. In general, such plates are made by "electrolytic etching" of a clean aluminum sheet with alternating current, usually in a hydrochloric acid solution, to grain, or etch, the surface. A thin cover layer of aluminum oxide is formed on the sheet during the etching. The sheet usually then is filled with a suitable filler material and coated with a light-sensitive substance capable of receiving a light-exposed image. The surface on such plates is not as hard as the surface obtained by the process of this invention, and it takes longer or requires more power to form a comparable surface because of the alternating current, which causes a sheet to act as both an anode and a cathode, and which makes spacing of the sheets critical. For these reasons, despite the state of the art, e.g., as reflected in those patents, to applicant's knowledge and in his experience it has not heretofore been possible to produce a commercially acceptable presensitized diazo anodized lithographic plate.

Accordingly, it is an object of this invention to provide an improved supporting base for lithographic plates. Another object of this invention is to provide an improved anodized aluminum supporting base for lithographic plates. Ir is also an object of this invention to provide improved presensitized anodized aluminum lithographic plates. Still another object of this invention is to provide an improved supporting base for presensitized and wipe-on lithographic plates that has exceptional inherent antihalation characteristics. These and other objects of this invention will be in part discussed and in part apparent in the more detailed disclosure hereinbelow.

It has been discovered that the foregoing objects can be achieved, and lithographic plates fulfilling those objects can be prepared, by electrolytically anodizing sheets of aluminum commonly used as base sheets for lithographic plates, which sheets previously have been

grained in a certain manner. In particular, aluminum sheets that are grained as disclosed herein and subsequently anodized have been found to be exceptionally superior as supporting bases for presensitized and for wipe-on lithographic printing plates. Other anodized aluminum sheets have dull, lustrous whitish matte finishes that tend to cause halation unless masked, for example, by a dye or other colored coating. Surprisingly, however, the finished surfaces of the grained and anodized aluminum sheets of this invention are quite different, being harder and of a dark grey, steel-like tone with little or no luster. Thus, lithographic printing plates of such grained and anodized aluminum plates have been found to be capable of producing as much as three times the number of copies as ordinary anodized or grained aluminum plates, and are substantially or entirely free of halation even without dyeing or other special treatment.

"Halation" in the reprographic art, and particularly in the lithographic art, connotes the phenomenon of imperfect light exposure onto the light-sensitive coated surface of a print or printing sheet caused by light passing through the coating and being reflected by the underlying supporting base back to the light-sensitive coating. The reflected light activates the coating and, because the reflected light is usually very dispersed, causes fuzzy, unsharp image boundaries resulting in poor quality prints, printing plates and copies printed with such plates. Both anodized and grained aluminum plates, although far less reflective than untreated aluminum, cause halation which ordinarily must be masked in one way or another, for example, by a dye or other colored material. The plates of this invention, however, inherently have little or no reflectivity and therefore cause virtually no halation so that clear, sharp images are obtained without the need of special masking treatment.

Methods of graining lithographic plate base sheets are known and commonly used. Plates can be grained in a variety of ways, including mechanically by rubbing with an abrasive, by sand blasting and by wire brushing, and chemically by treatment with various solutions. Thereafter, if desired, the plate can be mildly etched in a warm alkaline solution and rinsed. U.S. Pat. No. 2,882,154 and U.S. Pat. No. 2,882,153 describe more specifically ways of mechanically and chemically graining lithographic base sheets. Although graining tends to improve the bonding of the overcoated light-sensitive layer to the metal base, the grained metal surface is substantially unchanged in terms of its softness, susceptibility to corrosion, and reflectivity. Moreover, conventional brush graining and chemical graining do not, after anodizing, produce the hard, dark, lusterless surface obtained according to this invention. Similarly, conventional anodizing with alternating current in electrolytes such as hydrochloric acid does not produce the results of this invention.

I have found, however, that graining of an aluminum base sheet with a wet mass of fine hard abrasive particles followed by anodizing as disclosed below results in a remarkably distinct change in the character of the plate surface, namely, to a dark, steel-grey, lusterless nature that is hard and resistant to abrasion and corrosion, and that is virtually if not completely free from halation. Graining of the sheet can be done by hand or by machine, and requires only that the wet mass of particles be moved on the sheet surface an amount sufficient, considering speed and force, to create the fine scoring and roughening of the surface of a grained plate. Accordingly, the wet mass can vary in consistency from a dampened or moistened state to a slurry or suspension of the particles, depending on the particular mode of graining selected. The plate, after graining, is rinsed and if desired chemically cleaned prior to subsequent anodizing. The graining mass can be made up of a variety of fine, hard and abrasive particles. By hard and abrasive is meant materials that are harder than the aluminum surface to be grained so as to score and roughen the surface as applied thereto. A variety of materials are suitable for the purpose, including various silicates, oxides, sulfates and others, for example silicon dioxide as sand, aluminum, potassium and sodium silicates as pumice, aluminum oxide and magnesium sulfate minerals. Of such graining materials, pumice is preferred because of its availability, cost and efficacy.

After the base sheets have been grained, they are anodized. The sheets are the anodes in an anodizing tank in which sulfuric acid is the preferred electrolytic medium. The sulfuric acid solution strength preferably is in the order of about 15 percent by weight of acid in water, but can vary within a wider range, for example, between about 8 and about 22 percent, depending largely on practical and economic considerations. The electrolyte temperature does not appear to be critical, although at or slightly higher than ordinary room temperature seems to be sufficient and practically desirable. Agitation of the electrolye, for example, by a flow of air through it, also is desirable. Good results can be obtained using a voltage in the anodizing system of about 14 to about 15 volts, although a wider range of voltage can be used, e.g., from about 10 to about 20 volts. Preferably the area of the anodic sheet surface should be about the same as the surface area of the cathode. The latter surface can be a lead-lined tank or a lead coil which can also serve, along with air agitation, to cool the electrolytic solution. A fiberglass tank can be used. A current density of about 15 amperes per square foot of work is desirable, although the curent density also may vary within a wider range, for example, from about 10 to about 20 amperes per square foot. The anodizing time will vary depending on the foregoing factors. At the presently preferred conditions, i.e., about 15 percent sulfuric acid concentration, about 15 volts direct current, about 70° to 75°F. and about 15 amperes per square foot current density, good anodizing of grained aluminum sheets is obtained in about 2 minutes.

Because only one side of the sheet ordinarily is used as a lithographic surface, it is efficient to anodize two sheets simultaneously by tightly clamping them together so they act as a single anode and only their outer exposed grained surfaces are anodized. After anodizing the plates are rinsed, for example in cold water, for a brief period of time. Mild neutralizing solutions can also be used, if desired, prior to rinsing the plates.

The surfaces of the plates thus prepared have a metallic oxide coating that is very hard, abrasion resistant and porous. The surfaces, however, do not have the dull, lustrous, whitish matte finish either of anodized plates that have not been pre-grained or unanodized otherwise grained sheets. Instead, the surfaces surprisingly are much darker in color, a steel-grey or darker tone, and have little or no luster. Because of the porous

nature of anodized metal surfaces, such as the aluminum oxide on an anodized aluminum plate, it is common in the art to seal at least partially the anodized surface with various kinds of fillers that enter into the oxide coating and are retained therein, either or both chemically by reaction with the metal oxide or mechanically. Sealing is generally accomplished at elevated temperatures, at or near the boiling point of the sealing solution which can be simply water. With the pre-grained anodized plates of this invention, however, it unexpectedly has been found that sealing the anodized surface with fillers and the like is unnecessary.

On the other hand, it is desirable to treat the anodized surface, which is to receive the coating of a light-sensitive material, with an undercoating substance that forms a strong bond with the base sheet material and with the light-sensitive coating material. Many such undercoating treatments are known in the art and commonly used for longer-running lithographic plates, and can be used on the sheets of this invention. U.S. Pat. No. 3,160,506, U.S. Pat. No. 3,136,636, U.S. Pat. No. 2,946,683, U.S. Pat. No. 2,922,715 and U.S. Pat. No. 2,715,066 disclose a variety of suitable materials for undercoating bonding substances onto plates and methods for applying them. Alkali silicate, silicic acid, alkali zirconium fluoride and hydrofluozirconic acid solutions presently are the most important commercial bonding substances. Those materials substantially improve the bonding of the light-sensitive coating to the underlying metallic base which otherwise generally tends to have inadequate affinity for the coating. Of the various known bonding materials, the alkali zirconium fluorides, such as potassium zirconium hexafluoride, and hydrofluozirconic acid disclosed in U.S. Pat. No. 3,160,506 and U.S. Pat. No. 2,946,683 are especially satisfactory for preparing pre-grained anodized aluminum bases to receive a light-sensitive coating and are, therefore, preferred. The pre-coating treatment of the pre-grained anodized plates can be done according to the methods and under the conditions known in the art, as described in the above-mentioned patents, whose disclosures are specifically incorporated herein by reference.

It presently appears that the light-sensitive compounds and compositions known in the lithographic art as being suitable for coating onto aluminum bases are suitable for use on the pre-grained anodized base sheets according to this invention. Typical examples of such light-sensitive compounds and compositions include so-called tannable colloids, for example, albumin, casein, starch and synthetic film-forming resins such as polyvinyl alcohol and polyvinyl acetate that contain a dichromate sensitizer; photopolymerizable materials that are polymerized by photoinitiators such as carbonyl, organo-sulfur, peroxide and organo-halo containing compounds; diazo compounds such as diazobenzenes, diazonaphthalenes, diazo-aminobenzenes, diazo-diphenylamines and diazo-mercaptobenzenes; aromatic diazido compounds such as diazido-diphenylmethane carboxylic acids, azidostyrylketones, benzoquinone diazides, naphthoquinone diazides and resin-like esters of sulfonic acids of the latter with phenolformaldehyde or acetone-pyrogallol condensation produces; acenaphthenes; sulfanilido-methylene-fluorenes; S-alkylthiodiarylamine perchlorates; iodonitrothiophenes; and nitronaphthalenes, including carboxylic and sulfonic acid derivatives.

For making presensitized lithographic plates, certain of the above-mentioned kinds of light-sensitive compounds and compositions presently are preferred. They include generally the diazo compounds, and more particularly diazo-diphenylamine, substituted diazo-diphenylamine, condensation products of diazo-diphenylamines with compounds having reactive carbonyl groups, such as formaldehyde and paraformaldehyde, and unresinified light-sensitive reaction products of diazo-diphenylamine or condensation products thereof with hydroxyl-containing aromatic coupling agents; esters of diazo-naphthol sulfonic acids with condensation products of pyrogallol and acetone; and condensation products of quinone-(1,2)-diazide sulfonic acid halides with phenolformaldehyde resins.

Although the making of lithographic plates according to this invention will be apparent to persons skilled in the art from the foregoing disclosure, the following specific example is set forth to illustrate the preparation of a pre-grained anodized aluminum presensitized lithographic plate as one form of the invention.

Two aluminum sheets 10 inches by 15 inches and 0.005 inch thick are degreased and cleaned in a mild solution of sodium hydroxide and then brushed with a slurry of pumice until one surface of each sheet is uniformly grained. The grained sheets are then washed and clamped firmly with their ungrained surfaces together in an anode-bar rack. The sheets are immersed and anodized in a 70°–75°F. solution of 15 percent sulfuric acid by weight in water at 14.5 volts and direct current density of about 15 amperes per square foot for 2 minutes. The sulfuric acid solution is agitated by a flow of air through it. Thereafter the sheets are taken out of the rack and rinsed by dipping in cold water for 30 seconds. The grained and anodized surfaces have a dark, steel-grey, lusterless appearance, are hard and are resistant to abrasion. The sheets are then immersed in a 1 percent by weight solution of potassium zirconium hexafluoride at about 150°F. for 3 minutes, removed and allowed to drain for 1 minute, and immersed in water at about 150°F. for 3 minutes. After drying, the sheets are uniformly coated successively with a diazo compound that is the condensation product of paraformaldehyde and para-diazo-diphenylamine and then with a weak solution of 2,2',4,-4'-tetrahydroxy-benzophenone to form an unresinified, light-sensitive reaction product, e.g., as disclosed in U.S. Pat. No. 3,300,309. The coated sheets are dried, and the presensitized lithographic plates thus prepared can be exposed to light through an image, developed and run on a press.

Plates made as described have excellent lithographic characteristics, are free from halation, and provide press runs substantially greater than corresponding plates whose bases are either not pre-grained or not anodized.

The prolonged press-life of plates made according to this invention presently appears to be due to several factors. pre-graining and anodizing of the aluminum surface in the manner described seem to produce a harder surface, due to anodizing a surface roughened by graining with the wet graining mass, that is more abrasion resistant, wears longer and reduces wearing of the printing rolls against the image area. Also, that surface appears to be more porous, thereby providing better mechanical bonding of the intermediate and light-sensitive layers coated on it. Because of the inherent

antihalation character of the surface created in this way, the plate can be more fully exposed, without fear or halation, to achieve optimum insolubilization and hardening of the image which will run longer.

It is of course to be understood that the foregoing example is intended to be illustrative of the invention described, and that numerous changes can be made in the ingredients, conditions and proportions set forth therein without departing from the scope of the invention as disclosed above and defined in the claims appended hereafter.

I claim:

1. A method for making an aluminum supporting base adapted to receive a light sensitive coating thereon to make a lithographic plate which comprises first graining a surface of an aluminum sheet with a wet graining mass comprised of fine abrasive particles of pumice, and then anodizing the grained surface of said aluminum sheet in a sulfuric acid solution having a concentration of about 8 to about 22 percent, by a direct current applied at a voltage of about 10 to 20 volts and at a current density of about 10 to about 20 amperes per square foot, to form a hard, substantially lusterless surface on said sheet.

2. The plate produced in accordance with the method of claim **1.**

3. The method of claim **1** which comprises, further treating the grained and anodized surface of said aluminum sheet with an undercoating bonding substance to improve the bonding to said sheet surface of a light-sensitive lithographic composition to be received thereon.

4. The method of claim **3** wherein said undercoating bonding surface is directly applied to said anodized surface.

5. The method of claim **1,** wherein said sulfuric acid solution has a concentration of about 15 percent, said voltage is about 15 volts, and said current density is about 15 amperes per square foot.

6. The method for making an aluminum supporting base adapted to receive a light sensitive coating thereon to make a lithographic plate, which comprises;

a. First graining a surface of an aluminum sheet with a wet graining mass comprised of fine abrasive particles of pumice;

b. After said graining, chemically cleaning said aluminum sheet; and

c. Then anodizing the thus chemically cleaned grained surface of said aluminum sheet in a sulfuric acid solution having a concentration of from about 8 to about 22 percent by a direct current applied at a voltage of about 10 volts to about 20 volts and at a current density of about 10 amperes to about 20 amperes per square foot, to form the desired hard, substantially lusterless surface on said sheet.

7. The method according to claim **6,** wherein said sulfuric acid solution has a concentration of about 15 percent, said voltage is about 15 volts and said current density is about 15 amperes per square foot.

8. The method of claim **6** which comprises, further treating the anodized surface of said aluminum sheet with an undercoating bonding substance to improve the bonding to said sheet surface of a light-sensitive lithographic composition to be received thereon.

9. The method of claim **8** wherein said undercoating bonding surface is directly applied to said anodized surface.

10. The method of claim **6,** wherein the plate is chemically cleaned by mildly etching in a warm alkaline solution.

11. The plate produced in accordance with the method of claim **6.**

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