Aug. 8, 1972 J. W. KRUEGER 3,682,636
PRESENSITIZED PHOTOLITHOGRAPHIC PLATE HAVING
DIAZO STABILIZED ALUMIUM BASE
Original Filed Oct. 13, 1966

FIG.1

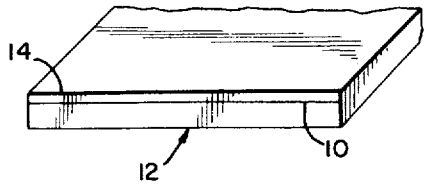


FIG.2

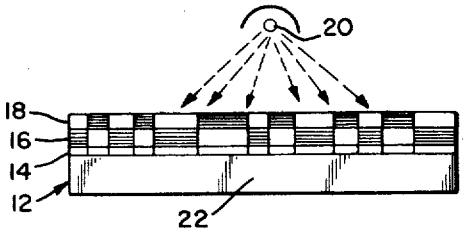


FIG.3

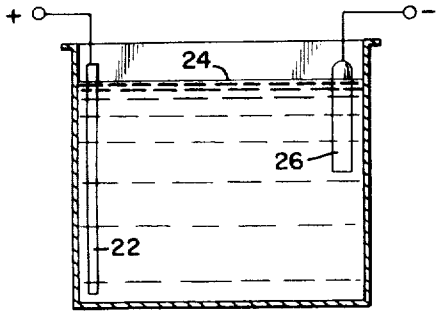


FIG.4

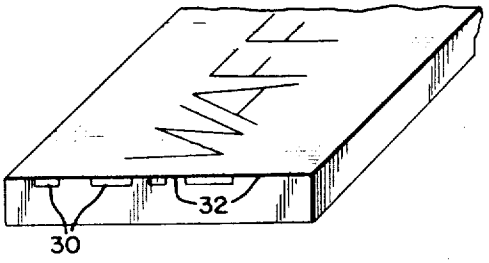
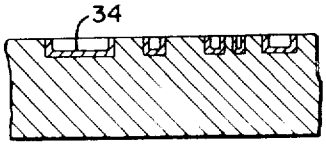


FIG.5



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PRESENSITIZED PHOTOLITHOGRAPHIC PLATE HAVING DIAZO STABILIZED ALUMINUM BASE

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Original application Oct. 13, 1966, Ser. No. 586,442. Divided and this application Nov. 12, 1970, Ser. No. 88,688

Int. Cl. G03c 1/52, 1/64, 1/66

U.S. Cl. 96—75 4 Claims

This application is a division of my copending application Ser. No. 586,442, filed Oct. 13, 1966, now U.S. Pat. 3,562,119, and entitled "Presensitized Aluminum Photolithographic Etched Plate and Elements and Method Used in the Preparation of Same."

This invention relates to a presensitized aluminum lithographic plate and to the method for producing same and to the method of use to produce a new and improved aluminum litho-etch plate from which multiple copies of excellent quality can be produced and it relates more particularly to a diazo sensitized aluminum lithographic plate and to the method of producing and using same.

To the present, in the preparation of a diazotized aluminum lithographic plate, it has been necessary to stabilize the lithographic surface against decomposition of the light sensitive, diaze resin forming compound, as by treatment of the surface to provide a silicated lithographic surface, as described, in the Jewett et al. Pat. No. 2,714,-066, or by pre-treatment of the surface with a polyacrylic acid polymer, as described in the Dowdall Pat. No. 3,136,-636. The stabilized surface is then provided with a coating of a water soluble, light sensitive resin forming diazo compound which, upon exposure, is reduced in the exposed areas to a resinous oelophilic, ink receptive compound which represents the ink receptive, water repellent image, while the diazo compound in the unexposed areas is removed by an aqueous wash, or preferably by the desensitizing solution to expose the underlying water receptive, lithographic surface which represents the non-imaged portions of the plate.

The ink receptive, water repellent imaging material forms on the surface of the plate in the exposed portions while the unexposed portions remain water receptive and hydrophilic. The plate can be mounted on a conventional lithographic press for the production of multiple copies by conventional lithographic duplicating technique. The number of copies that can be produced from plates of the type described is somewhat limited by the wear of the exposed image on the surface of the plate with the result that the imaged plate cannot be employed as a printing plate in the production of long run lithography.

Since the image formed on the surface of the plate is one characterized as having surface phenomenon, the amount of ink retained on the surface for transfer remains relatively constant in all of the exposed portions of the plate so that toned copies are incapable of being produced with presensitized plates of the type described.

It is desirable to provide a metal plate from which many thousands of copies of good quality can be produced and which is capable of being imaged by photographic technique to constitute a photolithographic printing plate and it is an object of this invention to produce an aluminum lithographic plate of the type described, and it is a related object to provide a method for producing same and for use of same in the preparation of an etched aluminum lithographic plate in which a permanent image is formed in the etched portions of the plate whereby the image is not subject to deterioration or wear and whereby the depth of the etch formed in the surface of the plate can be varied in response to the intensity of the original for corresponding variation in the amount of ink taken up by the image portions of the plate.

More specifically, it is an object of this invention to produce and to provide a method for producing a new and improved diazo sensitized aluminum lithographic plate and to produce and to provide a method for producing a new and improved deep etch lithographic plate therefrom; in which the presensitized aluminum lithographic plate has good stability and good shelf life; in which the plate can be imaged by exposure to an original for the production of an offset plate or to a negative transparency for the production of a direct image plate; in which the etched image portion can be plated with an ink receptive, water repellent metal to render the image portion even more oleophilic and to provide a still more permanent image from which many hundreds of thousands of copies can be produced.

These and other objects and advantages of this invention will hereinafter appear and for purposes of illustration, but not of limitation, an embodiment of the invention is shown in the accompanying drawing, in which:

FIG. 1 is a perspective view, partially in section, of a diazo sensitized aluminum lithographic plate prepared in accordance with the practice of this invention;

FIG. 2 is a sectional elevational view of the arrangement of elements for exposure of the diazo sensitized aluminum litographic plate of FIG. 1;

FIG. 3 is a schematic view of the arrangement of elements for electrical etch of the exposed plate of FIG. 2;

FIG. 4 is a perspective view, partially in section, of the etched lithographic plate produced in FIG. 3; and

FIG. 5 is an enlarged perspective view, partially in section, of a modification in the etched lithographic plate of FIG. 4 in which the imaged portion is plated with an ink receptive, water repellent metal.

A number of unexpected phenomena, which amount to important discoveries, are involved in the fabrication of the diazo sensitized aluminum lithographic plate of this invention, including the capability of imaging from a negative by photographic means and the preparation of a deep etch lithographic imaged plate from the exposed plate whereby a photolithographic printing plate is made available for the printing industry.

One such discovery resides in the preparation of a diazo sensitized aluminum lithographic plate capable of imaging by photographic technique. To the present, it was believed necessary to effect treatment of the surface of the aluminum plate to effect stabilization, as by silicating, before coating the treated surface with a light sensitive diazo resin or resin forming compound.

It is believed that an oxide of aluminum forms almost immediately on the surface of the aluminum plate and that the silicate treatment operates to bring about a reaction between the silicate and the aluminum oxide on the surface to form a hydrophilic layer of an aluminum oxide-silicon oxide which represents the lithographic surface and an which the light sensitive diazo resin compound is deposited with the aluminum oxide-silicon oxide layer functioning as a barrier to prevent decomposition or deterioration of the diazo compound applied to the surface thereof.

It has been discovered that when the light sensitive diazo resin or resin forming compound is applied in direct combination with the aluminum, as distinguished from the aluminum oxide otherwise present on the aluminum surface, a stabilized combination is formed in which the light sensitive resinous base diazo compound retains its light sensitivity for use as an imaging material over a very long period of time whereby a stable diazo presensitized aluminum lithographic plate can be produced without the surface treatments heretofore required to prestabilize the surface or to provide an intermediate barrier on which the diazo compound can be applied. It is belived that the diazo compound react with the nascent aluminum to form a stable diazo-aluminum compound in which the diazo compound retains its sensitivity to light and thus retains the properties required for producing an imaged master in response to exposure to a modulated light pattern corresponding to the image.

In the preferred practice of this invention, the described conditions for effecting a stable diazo-surface on the aluminum plate are effected by the incorporation of the diazo compound as an ingredient in a composition with which the surface of the aluminum plate is abraded or otherwise processed to effect removal of the oxide layer and to expose the raw aluminum to the diazo compound for stabilization or reaction. For this purpose, the light sensitive diazo resin or resin forming compound is formulated as a component in combination with rose tripoli or other abradant which is stable to the diazo compound, such as silica dust, glass dust, pumice and the like, as represented by the following example.

EXAMPLE 1

Diazo solution:

5 parts by weight p-diazodiphenylamine sulfate-formaldehyde condensate (Diazo Resin No. 4—Fairmont Chemical Company)
85 parts by weight water
25 parts by weight methanol

Scouring paste:

1 ounce rose tripoli
30 cc. diazo solution.

The surface **10** of the aluminum plate **12** is rubbed or scoured with the paste to free the aluminum from the oxide on the surface and to form a presensitized surface **14** with the diazo compound which remains stable over long periods of time and which remains light sensitive for exposure.

The surface **14**, after scouring, is not dried but is preferably washed with the diazo solution. If suitable precautions are taken, such as working in an inert atmosphere or under an inert gas, the abraded aluminum can be washed with water before sensitizing. Although less desirable the aluminum surface can be washed with water and sensitized before drying. In a preferred method, the abraded aluminum is protected from the oxygen in the air as much as possible. It is therefore contemplated to make use of antioxidants, such as thiourea during the process.

The rose tripoli in the above example can be replaced, in whole or in part, with other inert scouring agents such as pumice, silica dust and the like abrading materials which are inert to the diazo compound.

Other light sensitive diazo resins can be employed instead of the p-diazodiphenylamine sulfate-formaldehyde condensate of Example 1, such for example as aromatic azido resins and aliphatic azido resins or resins of the type described in the book entitled "The Aromatic Diazo Compounds," by H. K. Saunders, 1949, published by Edward Arnold & Company of London (p. 29); or monomolecular imino-quinone diazides; p-tertiary amino diazo resins are also useful, as well as the light sensitive diazo resins or resin forming compounds of the type described in the Jewett et al. Pat. No. 2,714,066. Also use can be made of the parent substance of the diazo resin such as the p-diazophenylamine sulfate and preferably its formaldehyde reaction product.

The amount of light sensitive diazo resin in the diazo solution can be varied over a fairly wide limit, consistent with the ability to form a paste with the scouring material in which sufficient of the diazo resin is present for the combination with the aluminum as it is exposed. Thus the concentration of the diazo resin in the solution can be varied up to as much as 25% but it is preferred to make use of between 0.25% to about 10% by weight of the solution and the ratio of the light sensitive diazo resin to the scouring medium can be varied over a fairly wide range such as within the range of one part by weight of diazo resin to 2–50 parts by weight of the rose tripoli or other scouring medium. It is preferred to work with a paste for efficient abrasion and continuous coverage with diazo solution. Thus additions of solution or abradient can be made from time to time.

The plate prepared in accordance with the proceding example is stabilized against the decomposition of the diazo resin compound so that additional amounts of diazo resin can be applied from solution onto the stabilized surface, depending somewhat upon the use to be made of the plate. The plate can be used as a presensitized photolithiographic plate in the same manner as described in the aforementioned Jewett et al. patent, by exposure through a negative transparency or to a positive whereby the diazo in the exposed portions is converted to an ink receptive, water repellent, water insoluble imaging material which remains strongly anchored to the surface of the plate, while the diazo resin in the unexposed portions can be washed from the surface of the plate by the developing solution to expose the underlying lithographic, water receptive, hydrophilic, non-imaged areas of the plate.

The exposed and developed plate can be mounted on a lithographic printing press for use in the production of a large number of copies of good quality. The plate that is produced is one that is characterized by the formation of the image on the surface, as in the Jewett et al. patent, but in which the surface constitutes a base which differs from that of the silicated aluminum oxide of the aforementioned patent. The adhesion of the image to the surface of the plate is outstanding.

While the described presensitized aluminum lithographic plate represents a new and novel plate embodying the features of this invention, it is employed primarily as the base for use in the preparation of a litho-etch plate, representing the preferred concepts of this invention.

In the preparation of a litho-etch plate, it is desirable to make use of a layer of the light sensitive diazo resin or resin forming compound having considerably greater thickness than will suffice for the preparation of a presensitized photolithographic plate of the type heretofore described.

For this purpose, it is desirable to incorporate a higher concentration of the light sensitive diazo resin in the scouring composition in order to deposit a higher concentration of diazo resin on the surface. In the preferred practice, one or more additional layers **16** of diazo resin is deposited on the diazo stabilized aluminum surface **14**.

The desired thickness of light sensitive diazo resin coating can be achieved by treatment of the diazo stabilized surface on the aluminum plate with a solution of the diazo resin in water and alcohol having a concentration within the range of about 1–10% by weight and preferably about 3–8% by weight of the light sensitive diazo resin solids, as represented by the following example.

EXAMPLE 2

	Percent
Light sensitive diazo resin (Fairmount No. 4)	5
Methanol	20
Water	75

The solution can be flow coated or roller coated onto the surface **14** of the diazo stabilized aluminum plate and then air dried or drying can be accelerated with hot air at an elevated temperature below the decomposition temperature for the diazo resin and preferably at a temperature of about 50° C.

The formed litho-etch plate can be stored in the dark for a relatively long period of time without deterioration of the light sensitivity of the plate.

In use, in the preparation of a litho-etch plate, a negative transparency **18** is positioned on the sensitized surface of the aluminum plate and exposed to a carbon arc lamp **20** of 110 volts and 20 amps at a distance of 24 inches for about 10 minutes. Other exposure techniques, well known to the art, can be employed, as by exposure to xenon pulsed lamps and the like, and the exposure can be made through a negative transparency, positive transparency, or by direct exposure, using photographic technique.

The exposed plate is then subjected to an electrical etch in which the exposed plate **22** is imersed in the electrolyte **24** as the anode while use is made of a zinc rod or plate **26** as the cathode, as represented by the following example.

EXAMPLE 3

Electrolytic bath:

Zinc chloride	pound	1
Water	gallon	1

With the exposed plate **22** suspended in the electrolyte **24** as the anode, and with a zinc plate **26** suspended in the bath as the cathode, a current of about 1–2 volts and about 1–2 amps is supplied for from 3 to 15 minutes.

A surprising feature of this invention resides in the discovery that the electrical etch occurs through the light exposed oleophilic, hydrophilic layer rather than the unexposed hydrophilic areas to yield a deep etch well containing the oleophilic image. To my knowledge this phenomenon has never heretofore been described nor even discussed as a possibility. This discovery has these consequences in the photomechanical imaging of metals. (1) All deep etch lithographic processes require that a positive original be used to produce a positive image; in contrast our deep etch process can use the negative directly from the camera and thus avoids the reversal step in the preparation of an original and the ordinary deep etch step in which large open areas must be staged. (2) All deep etch processes on single metal plates yield clear wells which must be made oleophilic without rendering unetched areas oleophilic; in contrast to this, our process can yield oleophilic wells.

The intensity of the current and the time of etch can be varied over fairly wide limits but in which the upper limit is defined by the time or intensity at which an etch begins to appear in the production of the plate surface underlying the unexposed portions of the plate.

When removed from the electrolytic cell, the electrolyte should be washed from the surface of the plate with alcohol, or less desirably with water, for complete removal and for more rapid drying of the plate surface.

The surface of the plate may be then treated with a desensitizer of the type conventionally employed in lithographic duplication, such as the Addressograph-Multigraph desensitizer, with or without previous lacquering of the surface of the plate. The desensitizer is applied preferably with rubbing with a cotton pad or the like to remove the diazo resin from the surface of the plate. The plate may be inked or lacquered either before or after desensitizing, or the oleophilic image left after the etching step may be used as such.

The resulting plate, however processed, is strongly hydrophobic in the etched portion **30** and hydrophilic in the unetched, non-imaged portions **32** of the plate. Thus the plate can be mounted on a conventional lithographic press for wetting sequentially by aqueous fountain solution, to wet out the non-imaged portions of the plate, and then by oleaginous ink, to wet out the etched imaged portions of the plate for transfer of the ink image from the plate to an offset blanket or directly to copy sheets.

By reason of the formation of the image as wells which extend into the surface of the metal plate, very little, if any, image wear will take place during use. As a result, the plate retains its image for the production of an endless number of copies and the plate can be reused any number of times, with periods of rest in between, without deterioration of the image.

Other electrolytes can be employed for the electrolytic etch. Such other electrolytes can be represented by aqueous solutions of salts such as sodium chloride, or combinations of sodium chloride and ammonium chloride, preferably in the ratio of 3 to 1, and present in concentrations to give a density of about 21 Bé. The time of exposure to the electrolytic etch will depend somewhat upon the intensity of the current and concentration of the salts making up the electrolyte solution.

This invention contemplates the further improvement in the permanency of the image and in the ink receptivity of the image by flash printing to form a layer of copper and the like hydrophobic metal as a lining in the wells formed by the etch. This can be accomplished, as by plating with a bath formed of an alkaline solution of copper sulfate, as represented by the following example.

EXAMPLE 4

Ethanolamine	grams	9
Copper sulfate	do	5.5
Water	cc	300
Gum arabic or other brightner	percent	1

The background, corresponding to the unetched or non-imaged portions of the plate, will not be copper-plated while the walls of the wells formed by the deep etch will receive a thin copper coat which renders the imaged portions permanently hydrophobic. The resulting plate constitutes an improved printing plate from which many hundreds of thousands of copies of good quality can be produced.

While the best results are secured when the light sensitive diazo resin is incorporated as a component in combination with the inert abradant to enable immediate stabilization by reaction or combination with the aluminum as it is freed by the abradant, a degree of stabilization sufficient for the production of a usable photolithographic plate can be achieved when the light sensitive diazo resin is applied for treatment of the aluminum surface independent of the abradant but substantially immediately following treatment of the surface to remove oxides normally formed on the surface, as by scouring with rose tripoli, pumice, silica, etc., wire brushing, rubbing as by kissing one surface with the other for self-abrasion, and the like. For this purpose, it is preferred to make application of the light sensitive diazo resin from aqueous alcohol solution or from a solution of water and acetone.

It will be understood that changes may be made in the details of formulation, treatment and use without departing from the spirit of the invention, especially as defined in the following claims.

I claim:

1. A diazo presensitized aluminum photolithographic printing plate consisting essentially of an aluminum base sheet and a diazo stabilized light sensitive aluminum surface formed by the combination of the diazo directly with the aluminum on the surface of the base sheet and a coating of a light sensitive, water soluble diazo resin on said diazo stabilized aluminum surface.

2. A diazo presensitized aluminum photolithographic printing plate as claimed in claim 1 in which the diazo resin is present in the coating on the surface in a concentration of more than 0.01 gram per 100 square feet of surface area.

3. A diazo presensitized aluminum photolithographic printing plate as claimed in claim 2 in which the diazo resin is present in the coating on the surface in an amount within the range of .02 to .1 gram per 100 square feet of surface area.

4. A diazo presensitized aluminum photolithographic printing plate as claimed in claim 2 in which the diazo resin is present in the coating in an amount greater than .01 but less than 1.0 gram per 100 square feet of surface area.

References Cited

UNITED STATES PATENTS

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DAVID KLEIN, Primary Examiner

U.S. Cl. X.R.

96—86, 33; 101—459, 463