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PRESENSITIZED DEEP ETCH LITHOGRAHIC PLATES

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This invention relates to deep etch lithographic plates which are presensitized and which retain their photographic sensitivity when stored for a prolonged period of time as well as to procedure for the preparation of such presensitized deep etch lithographic plates and more particularly to the use of a coating on at least one surface of such plates of a diazido-polyvinylpyrrolidone sensitizer.

The deep etch lithographic process is per se well known and is described in Publication No. 806 of The Lithographic Technical Foundation, Inc. (1954). It is also known that polyvinylpyrrolidone has been used in conjunction with diazonium sensitizers but has been found to be unsatisfactory as a deep etch resist because of the solubility characteristics of polyvinylpyrrolidone both in water and in organic solvents. This serious disadvantage has been obviated by the present invention wherein the polyvinylpyrrolidone is combined with polyacrylic acid or with other substances as hereinafter more fully set forth such as resorcinol or tannic acid. This combination is used in conjunction with the sodium salt of 4,4'-diazidostilbene-2,2'-disulfonic acid which is converted into its tetrazo form by means of sodium azide. Thus, in accordance with the present invention, a number of different formulations may be employed as diazido-polyvinylpyrrolidone based sensitizers. Four typical and entirely satisfactory formulations are as follows:

Formulation I:	Percent
Water (distilled)	94.25
Polyvinylpyrrolidone K–90	4.09
Polyacrylic acid (M.W. 95,000)	0.23
Sodium salt of 4,4'-diazidostilbene-2,2'-disulfonic acid	0.91
Sodium azide	0.30
Wetting agent	0.22
Formulation II:	
Water (distilled)	93.19
Polyvinylpyrrolidone K–90	4.47
Polyacrylic acid (M.W. 95,000)	0.51
Tannic acid	0.25
Sodium salt of 4,4'-diazidostilbene-2,2'-disulfonic acid	0.99
Sodium azide	0.33
Wetting agent	0.25
Formulation III:	
Water (distilled)	94.22
Polyvinylpyrrolidone K–90	3.92
Resorcinol	0.22
Sodium salt of 4,4'-diazidostilbene-2,2'-disulfonic acid	0.87
Sodium azide	0.33
Wetting agent	0.22
Formulation IV:	
Water (distilled)	93.67
Polyvinylpyrrolidone K–90	4.50
Tannic acid	0.25
Sodium salt of 4,4'-diazidostilbene-2,2'-disulfonic acid	1.00
Sodium azide	0.33
Wetting agent	0.25

Any suitable wetting agent can be employed, but it has been found that octyl phenoxy polyethoxy ethanol with an ethoxy chain length of 9 to 11 carbon atoms is particularly suitable and effective, and this wetting agent is available commercially as Triton X–100.

It is also pointed out that the proportions of ingredients in the above formulations are of critical significance and cannot be varied more than ±10% from the amounts specified above and that departures from the formulations of more than such permissible tolerance renders the formulations unsatisfactory or ineffective. This permissible variation applies to each ingredient individually. Each of the above formulations can be used to presensitize deep etch lithographic plates and the thus-produced plates retain their photographic sensitivity or solubility without undergoing any appreciable adverse change. Each of the formulations can be applied to various deep etch lithographic plates such as aluminum plates, zinc plates, magnesimum plates, stainless steel plates, copper electroplated aluminum bimetal plates, copper electroplated stainless steel bimetal plates, chromium electroplated copper bimetal plates, aluminum trimetal plates electroplated first with copper and then with chromium, and mild steel trimetal plates electroplated first with copper and then with chromium.

The above sensitizer formulations can be used interchangeably in all the succeeding examples without adversely affecting the qualities and performance of the presensitized plates. It is also to be understood that while the examples employ the whirlcoat method of application, the invention is not limited to any specific method of applying the sensitizers since it has been found further, for example, that a draw-down blade or a curtain coater can be equally well employed to apply the sensitizer to any of the above-noted plate surfaces.

Presensitized plates according to the present invention have been found to have a minimum storage life of at least six months and no maximum storage life has yet been encountered. Some plates were presensitized for eighteen months before final processing. This is an important commercial and operational advantage not shared by known presensitized plates. The presensitized plates of this invention have the further advantage over conventional lithographic plates in that the so-called "continuing dark reaction" is absent, this being the name given to the effect of continued insolubilization of a light-sensitive coating after termination of exposure. The continuing dark reaction effect prevents the exposing of portions of a conventional lithographic plate on different days and obtaining the same degree of insolubilization over the entire plate surface. In contrast, the presensitized plates of the present invention do not undergo the continuing dark reaction and this is especially important in step and repeat work inasmuch as no compensation has to be made in the exposure from the beginning to the end of the procedure. It will further be appreciated and understood that the present invention represents a marked and substantial advance in the art even though it includes certain phases of the invention of United States Patent No. 3,118,765.

The polyvinylpyrrolidone used has a K value between 88 and 94 and polyvinylpyrrolidone K–90 is particularly suitable in the present invention. The K values assigned to various grades of polyvinylpyrrolidone represent a function of the mean molecular weight and, for instance, polyvinylpyrrolidone K–90 has an average molecular weight of 360,000.

The polyacrylic acid is commercially available under the name "Good-Rite (K–702 Polymer)" and is a 25% aqueous solution of polyacrylic acid, which solution has a viscosity of 500 to 1200 centipoises, a specific gravity of 1.09, a pH value of 2 to 3, and a molecular weight in the range of 90,000 to 100,000 given above as 95,000.

The diazonium sensitizer is the sodium salt of 4,4'-diazidostilbene-2,2'-disulfonic acid produced by diazotizing 4,4'-diaminostilbene-2,2'-disulfonic acid and then neutralizing the reaction product with sodium carbonate. Sodium azide is then added to produce the tetrazo form of the above compound and this has the important significance of increasing the hardening action of the diazo compound upon the polyvinylpyrrolidone-polyacrylic acid admixture or reaction product or on the admixture or reaction product of polyvinylpyrrolidone with resorcinol or tannic acid. The tannic acid may, in addition, be utilized in conjunction with both polyvinylpyrrolidone and polyacrylic acid or the resorcinol or tannic acid may replace the polyacrylic acid.

The invention is illustrated by the following nonlimitative examples.

Example 1

A 17" x 22" x 0.012" sheet of ball grained 2S alloy aluminum is counteretched with a dilute aqueous solution of acetic acid and then rinsed thoroughly with tap water. The aluminum sheet is whirl coated with the deep etch positive sensitizer of formulation I above using conventional equipment and procedure. The sheet, after having been whirled dry, is exposed to a 13-amp. single carbon arc lamp at a distance of 40 inches for five minutes through a photographic positive. The sheet is then developed with the following developing solution which selectively dissolves the non-light struck portions of the coating:

	Grams
Water	32.88
$CaCl_2$	13.78
$ZnCl_2$	11.85
Hydroxyacetic acid (100%)	1.64
Ethylene glycol	38.84

The spent developing solution is removed from the plate with simultaneous removal of unhardened portions of the coating, after which the plate is ready for deep etching. The etching of the plate is accomplished by treating the unprotected portions thereof with the following etching solution:

$CaCl_2$ solution aqueous (40°–41° Bé.)	ml	1000
$ZnCl_2$	grams	380
$FeCl_2$ solution aqueous (50°–51° Bé.)	ml	285
HCl solution (37–38%) aqueous	ml	14
$CuCl_2 \cdot 2H_2O$	grams	27

The sheet is next washed with 99% isopropyl alcohol to remove the etching solution after the desired depth of etch has been reached. The plate is now treated with a solution which will chemically deposit copper metal onto the bare etched image areas. The composition of such a copperizing solution is:

Isopropyl alcohol (99%)	ml	1000
Cuprous chloride (Cu_2Cl_2)	grams	31
HCl (37–38.5%)	ml	32

The plate is again flushed with 99% isopropyl alcohol to remove the copperizing solution and to assist in removing moisture from the sheet surface which is fanned dry.

Next the sheet is coated with any of the commercial non-blinding deep etch lacquers which are usually vinyl based. The lacquering step is followed by an inking step which comprises coating the plate with a layer of commercial developing ink. The purpose of this step is to make the image apparent and to protect the lacquer layer from chemical attach. The plate is then flushed with warm water and brushed lightly to remove the resist and the lacquer and ink adhering thereto.

Thereafter the plate is desensitized by coating with a solution of phosphoric acid and gum arabic and when dried, moistened and inked, it is ready for printing.

Example 2

A 17" x 22" x 0.009" sheet of ball grained zinc is counteretched with a dilute aqueous solution of hydrochloric acid, then rinsed thoroughly with tap water. The zinc sheet is whirl coated with the deep etch positive sensitizer of Formulation I above, using conventional equipment and procedure. The sheet, after having been whirled dry, is exposed to a 13 amp. single carbon arc lamp at a distance of 40 inches for five minutes through a photographic positive. The sheet is then developed with the following developing solution which selectively dissolves the non-light struck portions of the coating.

	Grams
Water	32.88
$CaCl_2$	13.78
$ZnCl_2$	11.85
Hydroxyacetic acid (100%)	1.64
Ethylene glycol	39.84

The spent developing solution is removed from the plate with simultaneous removal of unhardened portions of the coating after which the plate is ready for deep etching. The etching of the plate is accomplished by treating the unprotected portions thereof with the following etching solutions:

	Grams
Water	45.99
$CaCl_2$	34.43
$MgCl_2$	15.30
Lactic acid (100%)	1.37
Formic acid (100%)	2.91

The sheet is next washed with 99% isopropyl alcohol to remove the etching solution after the desired depth of etch has been reached. The plate is now treated with a solution which will chemically deposite copper metal onto the bare, etched image areas. The composition of such a copperizing solution is:

Isopropyl alcohol (99%)	ml	1000
Cuprous chloride (Cu_2Cl_2)	grams	31
HCl (37–38%) aqueous solution	ml	32

The plate is again flushed with 99% isopropyl alcohol to remove the copperizing solution and to assist in removing moisture from the sheet surface which is fanned dry.

Next, the sheet is coated with any of the commercial non-blinding deep etch lacquers which are usually vinyl based. The lacquering step is followed by an inking step which comprises coating the plate with a layer of commercial developing ink. The purpose of this step is to make the image apparent and to protect the lacquer layer from chemical attack. The plate is then flushed with warm water and brushed lightly to remove the resist and the lacquer and ink adhering thereto.

Thereafter, the plate is desensitized by coating it with a solution of phosphoric acid and gum arabic and when dried, moistened and inked, it is ready for printing.

Example 3

A 10" x 15" x .020" sheet of magnesium is counteretched with a 5% aqueous solution of ammonium bichromate and pumice powder, then rinsed thoroughly with tap water. The magnesium sheet is whirl coated with the sensitizer of Formulation IV using conventional equipment and procedure. The sheet, after having been whirled dry, can be stored away for several months without any loss of photographic sensitivity or it is exposed to a 35 amp. double carbon arc lamp at a distance of 42 inches for five minutes through a photographic positive. The sheet is then developed with the following developing solution which selectively dissolves the non-light struck

portions of the coating and also etches the bared magnesium:

Water	ml	32.88
$CaCl_2$	grams	13.78
$ZnCl_2$	do	11.85
Hydroxyacetic acid (100%)	do	1.64
Ethylene glycol	do	39.84

The sheet is next washed with 99% isopropyl alcohol to remove the etching solution after the desired depth of etch has been reached.

Next, the dry plate is coated with any of the commercial non-binding deep etch lacquers which are usually vinyl based. The lacquering step is followed by an inking step which comprises coating the plate with a layer of commercial developing ink. The plate is then flushed with warm water and brushed lightly to remove the resist and the lacquer and the ink adhering thereto.

Thereafter the plate is desensitized by coating with a solution of phosphoric acid and gum arabic and when dried, moistened and inked, it is ready for printing.

Example 4

A 19¾" x 23" x .015" sheet of ball grained 316 stainless steel is counteretched with a dilute aqueous solution of hydrochloric acid, then rinsed thoroughly with tap water. The stainless steel sheet is whirl coated with the sensitizer of Formulation II, using conventional equipment and procedure. The processing of the plate was carried out in the same manner as in Example 2 with the exception that the copperizing solution is of the following composition:

Isopropyl alcohol (99%)	cc	450
Ethylene glycol	cc	450
Hydrochloric acid (37%)	cc	42
Cuprous chloride	grams	32

Example 5

A 20" x 22⅝" x .012" sheet of 0.0119 inch aluminum with a surface of 0.0001 inch electroplated copper is counter-etched with a dilute aqueous solution of sulfuric acid, then rinsed thoroughly with tap water. The copper electroplated aluminum sheet is whirl coated with the sensitizer of Formulation III using conventional equipment and procedure. The sheet, after having been whirled dry, can be stored away for several months without any loss of photographic sensitivity or immediately exposed to a 95 amp. single arc lamp at a distance 52 inches for five minutes through a photographic negative. The sheet is then developed with the following developing solution which selectively dissolves the non-light struck portions of the sensitizer:

Water	cc	32.88
$CaCl_2$	grams	13.78
$ZnCl_2$	do	11.85
Hydroxyacetic acid (100%)	do	1.64
Ethylene glycol	do	39.84

The spent developing solution is removed from the plate with simultaneous removal of unhardened portions of the sensitizer, after which the plate is ready for etching. The etching of the plate is accomplished by treating the unprotected portions thereof with the following etching solution which removes the bared copper but does not etch the underlying aluminum:

Ferric nitrate	grams	640
Water	cc	500

The plate is next flushed with warm water and brushed lightly to remove the resist from the copper areas of the plate. The plate now consists of aluminum non-printing areas which were not exposed to light and copper image areas which were protected during the etching step by the light-hardened sensitizer.

Thereafter the aluminum surface is desensitized by coating it with a dilute solution of gum arabic while the copper surface is made ink receptive by application of a dilute aqueous solution of sulfuric acid. The inked and desensitized plate is now ready for printing.

Example 6

Example 5 was followed except that the plate consists of 0.0001 inch copper electroplated directly on 0.0119 inch mild steel. The chemical solutions and procedure used are the same except for the etching solution which has the following composition:

Ferric chloride	grams	1000
Calcium chloride (80%)	do	1000
Water	cc	2000

Example 7

A 10" x 15" x .009" sheet of .00895 copper with an electroplated surface of .00005 inch chromium is counteretched with a dilute aqueous solution of phosphoric acid, then rinsed thoroughly with tap water. The chromium electroplated copper sheet is whirl coated with the sensitizer of Formulation II using conventional equipment and procedure. The sheet, after having been whirled dry, can be stored away for several months without any loss of photographic sensitivity or it can be exposed immediately to a 95 amp. single carbon arc lamp at a distance of 52 inches for five minutes through a photographic positive. The sheet is then developed with the following developing solution which selectively dissolves the non-light struck portions of the sensitizer:

Water	cc	32.88
$CaCl_2$	grams	13.78
$ZnCl_2$	do	11.85
Hydroxyacetic acid (100%)	do	1.64
Ethylene glycol	do	39.84

The spent developing solution is removed from the plate with simultaneous removal of the unhardened portions of the coating, after which the plate is ready for etching. The etching of the plate is accomplished by treating the unprotected portions thereof with the following etching solution which removes the bared chromium but does not attack the underlying copper:

Aluminum chloride, anhydrous	grams	450
Zinc chloride	do	630
Phosphoric acid (85%)	cc	40
Water	cc	700

The plate is next flushed with warm water and brushed lightly to remove the exposed sensitizer from the chromium areas of plate which will become the non-printing areas of the plate. The copper or printing areas of the plate consists of those areas which were not exposed to light and subsequently were etched free of chromium.

Thereafter the chromium surface is desensitized by coating it with a dilute solution of gum arabic while the copper surface is made ink receptive by applications of a dilute aqueous solution of sulfuric acid. The inked and desensitized plate is now ready for printing.

Example 8

A 19¾" x 23" x .012" trimetal plate composed of an aluminum base 0.012 inch thick electroplated with 0.0001 inch of copper which is electroplated with 0.00005 inch of chromium is sensitized and processed in the same manner as the plate of Example 7.

Example 9

A 20" x 22⅝" x .012" trimetal plate composed of a mild steel base 0.012" thick electroplated with 0.0001 inch of copper which is electroplated with 0.00005 inch of chromium is sensitized and processed in the same manner as the plate of Example 7.

What is claimed is:

1. A presensitized deep etch lithographic plate which retains its photographic sensitivity when stored for a pro-

longed period of time, comprising a metal plate having on at least one surface thereof a coating of a diazido-polyvinylpyrrolidone sensitizer composed of the following constituents in the following amounts with in a ±10% tolerance:

	Percent
Water (distilled)	93.19
Polyvinylpyrrolidone K–90	4.47
Polyacrylic acid (M.W. 95,000)	0.51
Tannic acid	0.25
Sodium salt of 4,4'-diazidostilbene-2,2'-disulfonic acid	0.99
Sodium azide	0.33
Wetting agent	0.25

2. A presensitized deep etch lithographic plate which retains its photographic sensitivity when stored for a prolonged period of time, comprising a metal plate having on at least one surface thereof a coating of a diazido-polyvinylpyrrolidone sensitizer composed of the following constitutents in the following amounts within a ±10% tolerance:

	Percent
Water (distilled)	94.22
Polyvinylpyrrolidone K–90	3.92
Resorcinol	0.22
Sodium salt of 4,4'-diazidostilbene-2,2'-disulfonic acid	0.87
Sodium azide	0.33
Wetting agent	0.22

3. A presentized deep etch lithographic plate which retains its photographic sensitivity when stored for a prolonged period of time, comprising a metal plate having on at least one surface thereof coating of a diazido-polyvinylpyrrolidone sensitizer composed of the following constituents in the following amounts within a ±10% tolerance:

	Percent
Water (distilled)	93.67
Polyvinylpyrrolidone K–90	4.50
Tannic acid	0.25
Sodium salt of 4,4'-diazidostilbene-2,2'-disulfonic acid	1.00
Sodium azide	0.33
Wetting agent	0.25

4. A presentized deep etch lithographic plate according to claim 1, in which the metal of the plate is selected from the group consisting of aluminum, zinc, magnesium, stainless steel, copper electroplated aluminum, copper electroplated stainless steel, chromium electroplated copper, aluminum electroplated first with copper and then with chromium and mild steel electroplated first with copper and then with chromium.

5. A presensitized deep etch lithographic plate according to claim 2, in which the metal of the plate is selected from the group consisting of aluminum, zinc, magnesium, stainless steel, copper, electroplated aluminum, cooper electroplated stainless steel, chromium electroplated copper, aluminum electroplated first with copper and then with chromium and mild steel electroplated first with copper and then with chromium.

6. A presensitized deep etch lithographic plate according to claim 3, in which the metal of the plate is selected from the group consisting of aluminum, zinc, magnesium, stainless steel, copper electroplated amluinum, copper electroplated stainless steel, chromium electroplated copper, aluminum electroplated first with copper and then with chromium and mild steel electroplated first with copper and then with chromium.

7. A presensitized deep etch lithographic plate according to claim 1, in which the wetting agent is octyl phenoxy polyethoxy ethanol with an ethoxy chain length of 9 to 11 carbon atoms.

8. A presensitized deep etch lithographic plate according to claim 2, in which the wetting agent is octyl phenoxy polyethoxy ethanol with an ethoxy chain length of 9 to 11 carbon atoms.

9. A presensitized deep etch lithographic plate according to claim 3, in which the wetting agent is octyl phenoxy polyethoxy ethanol with an ethoxy chain length of 9 to 11 carbon atoms.

10. A diazido-polyvinylpyrrolidone sensitizer for the production of presensitized deep etch lithographic plates, in which the sensitizer is composed of the following constituents in the following proportions within a ±10% tolerance:

	Percent
Water (distilled)	93.19
Polyvinylpyrrolidone K–90	4.47
Polyacrylic acid (M.W. 95,000)	0.51
Tannic acid	0.25
Sodium salt of 4,4'-diazidostilbene-2,2'-disulfonic acid	0.99
Sodium azide	0.33
Wetting agent	0.25

11. A diazido-polyvinylpyrrolidone sensitizer for the production of presensitized deep etch lithographic plates, in which the sensitizer is composed of the following constituents in the following proportions within a ±10% tolerance:

	Percent
Water (distilled)	94.22
Polyvinylpyrrolidone K–90	3.92
Resorcinol	0.22
Sodium salt of 4,4'-diazidostilbene-2,2'-disulfonic acid	0.87
Sodium azide	0.33
Wetting agent	0.22

12. A diazido-polyvinylpyrrolidone sensitizer for the production of presensitized deep etch lithographic plates, in which the sensitizer is composed of the following constituents in the following proportions within a ±10% tolerance:

	Percent
Water (distilled)	93.67
Polyvinylpyrrolidone K–90	4.50
Tannic acid	0.25
Sodium salt of 4,4'-diazidostilbene-2,2'-disulfonic acid	1.00
Sodium azide	0.33
Wetting agent	0.25

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