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[54] **SOLVENT DEVELOPMENT OF LIGHT-SENSITIVE
DIAZO LAYERS**
10 Claims, No Drawings

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[56] **References Cited**
UNITED STATES PATENTS
3,019,106 1/1962 Adams 96/48
3,406,065 10/1968 Uhlig 96/36.3
FOREIGN PATENTS
844,039 8/1960 Great Britain 96/36
784,001 10/1959 Great Britain

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ABSTRACT: The development of positive-working light-sensitive diazo layers for use as lithographic printing plates and photoresists is effected using selectively acting organic solvents to dissolve light-struck areas.

SOLVENT DEVELOPMENT OF LIGHT-SENSITIVE DIAZO LAYERS

BACKGROUND OF THE INVENTION

Positive-working light-sensitized lithographic plates are known and disclosed, for example, in U.S. Pat. Ser. Nos. 3,046,121 and 3,046,120 and in United Kingdom Pat. Specifications Nos. 739,654 and 1,034,191 according to which the sensitized layer comprises a diazo-oxide derivative. Such plates are also disclosed in U.S. Pat. No. 3,219,447 where the sensitized layer comprises a mixture of a diazonium derivative with an alkali-soluble novolak resin. The sensitized layer in each case may be applied to a metal such as an aluminum or zinc sheet. The image on such plates is developed by the use of alkaline developers which are not only unpleasant to handle but may have a corrosive effect on the areas of the plate laid bare by such development. This effect is particularly marked in the case of plates which have been chemically or electrochemically grained.

These alkaline developers have the further disadvantage that while the contents of a stock bottle are being used the alkalinity becomes reduced due to absorption of carbon dioxide from the air. This becomes very important in developing machines. This development is generally followed by treatment with an acid desensitizer.

The use of grained or anodized printing plates in lithography is well known as being desirable (e.g. see L. E. Lawson, *Offset Lithography*, Vista Books, London 1963). By graining or anodizing we mean the production of a finely textured matte surface on a metal printing plate and the work matte as used herein has reference to such treatment. So-called "scratch brushed" aluminum plates are also on the market. These are simple to produce by mechanical means, but do not meet all the requirements of the printer in practice. Grained and/or anodized printing plates exhibit an increased water wettability of the nonprinting area as well as permitting a better control over the amount of moisture present when printing. The action of the nonprinting areas is dependent on a desensitizing layer and the roughened surface assists in retaining this layer. In addition, graining or anodizing allows a considerable amount of wear to occur before the desensitized layer is seriously affected and furthermore, it promotes adhesion of the light-sensitive layer as well as of the final image. Above all, a grained or anodized plate is preferred by the printer for ease of use in that the balance between ink and water, i.e., the control of the fountain solution, is not so critical.

The application of the positive-working process using matte metal surfaces has in particular, as well as the possibility of corrosion mentioned above, the disadvantage that on development of the plate with an alkaline developer, the exposure products of the diazo oxides or diazonium derivatives may form a stain or dye in the nonimage areas with the possibility of retention of small particles in the pits of the grain of the matte surface, which makes the plate unacceptable to the printer because of the risk of ink-acceptance in the nonprinting areas of the plate.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a new process for the development of positive-working lithographic plates in which the use of an alkaline developer can be dispensed with.

We have now found unexpectedly that the alkaline developer may be dispensed with in the development of positive-working lithographic plates as described above and that one may simply use as developer a solvent for the layer in the nonimage areas, if desired combined with a lithographic desensitizer.

By the term positive working as used herein and in the appended claims we mean not only a positive image produced from a positive transparency but also positive resist processes where, according to the process, a negative transparency may be needed.

The use of solvent development according to the invention, besides the advantages mentioned above, also lends itself to the possibility of use of an emulsion of solvent and aqueous desensitizer solution, thus giving one solution processing for the plate, and to the possibility of a combined developer, desensitizer, and reinforcing lacquer. Furthermore it gives the possibility of use of a tough nonphotosensitive sublayer which is solvent soluble and which is removed in the nonimage areas by the developing agent but remains to reinforce the image areas. The means of development adopted may be any of those used in the trade such as swabbing, immersion in tank or dish, or use of a developing machine.

According to the invention therefore, we provide a process for the development of positive-working lithographic plates in which the exposed lithographic plate is treated with a solvent or mixture of solvents for the presensitized coating selectively to remove the layer from those areas which have been exposed, that is from the nonimage areas, the solvent or solution, if desired, containing a desensitizer.

The fact that it is possible to develop metal positive-working plates by this process is very surprising and was not to be expected on the basis of existing knowledge of positive-working lithographic plates. There is a previous reference to solvent development using aqueous alcohol or aqueous alcoholic calcium chloride in United Kingdom Pat. Specification No. 732,544, but in that case the image obtained turned out to be a negative copy of the original, as the solvent preferentially dissolved the unchanged, diazo-oxide, nonexposed, areas of the layer. The same result was obtained by the process of United Kingdom Pat. Specification No. 860,386 where use is made of tetralin combined with a gum-etch desensitizer. United Kingdom Pat. Specification No. 784,001 describes positive working plates based on diazo-oxides but its method is restricted to paper plates which have to be specially subbed and where the developers are restricted to aliphatic polyhydroxy compounds followed by the use of an alkanolamine to impart a hydrophilic character to the sublayer.

The actual solvent or solvents used as developer will be selected having regard to the particular type of positive-working lithographic plate and to the means of development used. This selection can be made by simple experiment and presents no difficulty. The selected solvent should be one which dissolves the layer at an appreciable rate in the nonimage areas, that is in exposed areas, while having no substantial effect on the remaining sensitive layer in the image areas. It should also preferably be a solvent which is cheap and commercially available as well as one which presents no difficulties in use, for example from the odor or toxicity point of view.

Preferred solvents are in general higher boiling organic solvents which are generally immiscible with water. Suitable classes of solvents include in particular aliphatic alcohols and ketones as well as organic esters.

2-ethyl hexanol,

1-octanol,

2,6-dimethyl-4-heptanone, 6-methyl-3-heptanone,

n-hexyl acetate,

diethylphthalate,

diethyl carbonate,

3-methyl-2-pentanone,

Industrial ethyl alcohol.

The solvents used according to the invention may be used in combination with desensitizer and if desired a lacquer or similar reinforcing or protecting agent may also be applied with the solvent so that after development an image is obtained in which the nonimage areas have been desensitized while the image has been coated with a protective lacquer. In adopting this procedure a suitable desensitizer, such as a gum-etch based for example on gum arabic, and phosphoric acid solution may be used combined in suitable proportions, for example 1:1 by weight with the selected solvent. An emulsifying agent may be added to this if desired. If a reinforcing lacquer is needed to be applied, for example a novolak resin or an epoxy resin, this may also be applied in solution in the selected developer. Finally it may be found to be advantageous to add a

dye or pigment to the developer to render the image more visible, or to add a photodesensitizing dye to render the image insensitive to light.

When a lithographic plate is being made the metal used may be selected from a number of possibilities, provided the surface can be rendered hydrophilic after scratch-brushing or preferably after graining and/or anodizing. The plate metal is preferably aluminum or zinc but this is not essential. When the coating is used as a photoresist many other substrates may be employed according to the process being carried out but the same means of development can be used to give good results with resists for use on e.g. multimetal plates, copper plates or cylinders. In some of these cases, a negative transparency may be needed to give a final positive printing image. In the case of printed circuit resists, a positive transparency or a negative transparency of the final circuit will be needed according to the process being used. The development process of the invention may also be used on electrophotographic or xerographic printing plates where the resin image is formed as a resist on a layer of alkali-soluble material which has to be removed in the nonimage areas, e.g., United Kingdom Pat. Specification Nos. 917,641 and 944,126.

The following examples illustrate the invention. In these examples the printing plates all have a diazo oxide or diazonium derivative-containing sensitized layer.

EXAMPLE 1

An Ozasol Aluminum Positive Printing Plate P4 a light-sensitive lithographic plate in which the light sensitive material is a quinone diazide sulphonic acid ester was exposed under a positive transparency and developed with 2-ethyl-hexanol as solvent by rubbing with a swab for 5 minutes; after removing excess solvent, the plate was rubbed with commercial gum-etch solution, rinsed and dried well by means of hot air, when it was ready to use in a printing machine. Similar satisfactory results were obtained when 1-octanol, 2,6-dimethyl-4-heptanone, and diethyl phthalate were used as solvent; in the case of the last 2 solvents development was faster than with ethyl-hexanol or 1-octanol but care had to be taken not to keep the plate in contact with the developer after development was complete to avoid damage to the image area. Similarly 2-ethyl hexanol may be used with an Ozasol Positive Printing Plate P6, a light-sensitive lithographic plate in which the light sensitive material is a quinone diazide sulphonic acid ester.

EXAMPLE 2

A Ferrania Presensitized Offset Plate, light-sensitive lithographic plates in which the light-sensitive material is a quinone diazide sulphonic acid ester, was exposed under a positive transparency. It behaved in the same way with the solvents given in example 1.

EXAMPLE 3

An Ozasol Chromium on Brass N5 Plate light-sensitive lithographic plates in which the light sensitive material is a quinone diazide sulphonic acid ester, was exposed under a negative transparency and developed with 2-ethyl hexanol, wiped off, dried, and etched with a hydrochloric acid etch to lay bare the oleophilic metal in the image areas. The resist was then removed from the chromium areas which are hydrophilic by means of a solvent such as 2-ethoxyethanol.

EXAMPLE 4

The plate of example 1 was developed with a mixture of equal parts of 2-ethyl hexanol and a solution of 30 percent gum arabic, 5 percent mono-ammonium phosphate, 5 percent orthophosphoric acid, and 0.25 percent Permal BX (Imperial Chemical Industries Ltd), the sodium salt of an alkylated naphthalene sulphonic acid. After rinsing and drying it was ready for the printing press. The Ozasol Plate P6 behaved similarly.

EXAMPLE 5

A solution of 2 percent 4'-methoxy-diphenylamine-4-diazonium chloride and 10 percent novolak (Pioneer Resin 429-Fredk. Boehm Ltd produced by condensing formaldehyde with o-cresol) in 2-ethoxyethanol was coated on to a grained aluminum plate in a plate-whirler and when dry was stoved for 2 minutes at 100° C. After exposure under a screened positive transparency it was successfully developed with 6-methyl-3-heptanone following the procedure of example 1. Similarly, may be used, 2,6-dimethyl-4-heptanone, 1-hexyl acetate and diethyl carbonate. When a similar plate was developed with 3 percent trisodium phosphate solution, a stained background was obtained.

EXAMPLE 6

An exposed plate obtained as in example 5 was developed with the emulsion developer of example 4 with successful results. Similar results were obtained with an emulsion of 2,6-dimethyl-4-heptanone in place of 2-ethyl hexanol.

EXAMPLE 7

A plate prepared and exposed as in example 5 was developed with an emulsion containing 50 ml. 2,6-dimethyl-4-heptanone and 50 ml. of an aqueous solution of 1 percent sodium metasilicate and 2½ percent of the hydrophilic colloid known as Gantrez-half amide (General Aniline and Film Corporation, New York), or Gantrez AN4141 which is the half amide of a copolymer of methyl vinyl ether and maleic anhydride to give a satisfactory printing plate.

EXAMPLE 8

0.5 g. of the diazo resin p-toluene sulphonate prepared as in United Kingdom Pat. Specification No. 944,276 was dissolved in a mixture of 5 ml. water and 5 ml. formdimethylamide and added to 40 ml. of a 10 percent solution of novolak in 2-ethoxyethanol. This solution was coated on to a grained aluminum plate which was stored at 100° for 1 minute after it had dried. It was exposed under a positive transparency and developed with 2,6-dimethyl-4-heptanone and then gum etched to give a positive printing plate. In this case, use of an emulsion developer was unsuccessful.

EXAMPLE 9

2 g. of the bis-[naphthoquinone-(1,2)-diazide-(2)-5-sulphonic acid ester] of 4,4'-dihydroxy-diphenyl-sulphone and 2g. PR429 (Pioneer-resin 429) novolak were dissolved in a mixture of 50 ml. formdimethylamide and 50 ml. 2-ethoxyethanol and a plate of grained and anodized aluminum was coated with the solution using a whirler. When dry, the plate was exposed under a positive to the light from a carbon-arc lamp developed with 2-ethyl hexanol, gum-etched and inked in to give a printing plate free of stain in nonimage areas.

EXAMPLE 10

The naphthoquinone (1,2)-diazide-(2)-5-sulphonic acid ester of novolak PR429 (see U.K. Pat. Specification No. 711,626) was made up as a 2 percent solution in 2-ethoxyethanol and coated on to a grained aluminum plate. After exposure under a positive it was developed with industrial alcohol to give a printing plate.

EXAMPLE 11

A plate coated as in example 5 was exposed under a positive and developed by means of an emulsion prepared from 20 g. Pioneer Resin, 429, 1 g. Methyl Violet, 60 ml. 2,6-dimethyl-4-heptanone and 60 ml. gum etch. The result was a developed and desensitized lithographic plate, bearing on the image a resin reinforcement to give a longer printing run.

EXAMPLE 12

A grained aluminum plate was coated at 0.5 g./m.² with a sub layer of Vinylite Resin VYHH (Bakelite Ltd., London) a copolymer of vinyl chloride, from a 5 percent solution in Butoxyl (methoxybutyl acetate) and this, after drying, was coated using the solution of example 5, to give a total coating weight of 4 g./m.². After exposure under a positive and development with 2,6-dimethyl-4-heptanone, the plate was dried and gum-etched to give a plate which, while having a short exposure time, had a very long printing life.

EXAMPLE 13

Copper foil laminated to resin impregnated board as used in production of printed circuits was coated using the solution of example 5, and when dry was heated for 2 minutes at 100°. After exposure under a positive pattern of the design of an electronic circuit, the board was developed with 6-methyl-3-heptanone, dried and the exposed area of copper etched away with ferric chloric solution. After this the board was rinsed and the resist removed with 2-ethoxyethanol leaving the required copper circuit.

EXAMPLE 14

The procedure of example 13, was followed except that a negative pattern of the circuit was used. The developed board is electroplated with silver and after rinsing and removal of the resist from the nonexposed areas, the copper areas laid bare were removed by means of a ferric chloride etch to leave the desired circuit as silver-plated copper.

EXAMPLE 15

A plate coated as in example 9 was exposed under a negative transparency and developed by wiping over with 2-ethylhexanol using a swab of cotton wool. After rinsing with fresh solvent the plate was thoroughly dried and then etched with the "deep-etch" solution sold in the trade as Deep-Etch 'U'—Algraphy Limited, an etch for aluminum which is based on zinc chloride, for 4 minutes. After rinsing with water and drying the plate was lacquered in the image areas with a solution of 8 percent Epikote 1001 Resin (Shell Ltd.) an epoxy resin in 60 percent Mesitylene, 40 percent Xylene, including 0.5 percent oil-soluble blue dye. After drying the plate was given a fogging exposure with a carbon-arc lamp, the stencil removed with 1 percent sodium hydroxide solution and the plate gummed up ready for the press.

EXAMPLE 16

A plate coated as in example 5 was exposed under a negative transparency and developed by wiping over with 2,6-dimethyl-4-heptanone using a swab of cotton wool. After rinsing with fresh solvent, the plate was thoroughly dried and then etched with the "deep-etch" solution sold in the trade as

Deep-Etch 'U'—Algraphy Limited for 4 minutes. After rinsing with water and drying the plate was lacquered in the image areas either with "Patralac," a deep etch lacquer which contains a copolymer of vinyl chloride, or with a solution of the Vinylite Resin VYHH (Bakelite Ltd.) 10 percent in 2,6-dimethyl-4-heptanone containing 0.5 percent oil-soluble blue dye. After drying the plate was given a fogging exposure with a carbon-arc lamp, the stencil removed with 5 percent trisodium phosphate solution and the plate gummed up ready for the press.

We claim:

1. Process for the development of imagewise exposed photosensitive material coated in a layer on a support in admixture with an alkali-soluble resin and selected from the group consisting of diazo-oxides and diazonium derivatives, which process comprises treating the exposed layer with a developer comprising a nonalkaline phase containing a water-immiscible organic solvent for the light-struck areas of the material to selectively dissolve the light-struck areas of the material, said solvent being selected from the group consisting of aliphatic alcohols and ketones, and organic esters.

2. Process in accordance with claim 1, wherein the developer includes a desensitizer to render hydrophilic the underlying areas of the support revealed on selective removal of the light-struck areas.

3. Process in accordance with claim 1, wherein the developer is in the form of an aqueous emulsion.

4. Process in accordance with claim 1, wherein said organic solvent is selected from the group consisting of 2-ethylhexanol; 1-octanol; 2,6-dimethyl-4-heptanone; 6-methyl-3-heptanone; 3-methyl-2-pentanone; n-hexyl acetate; diethyl phthalate and diethyl carbonate.

5. Process in accordance with claim 1, wherein the developer includes a resin which is deposited on the nonlight-struck areas during development.

6. Process in accordance with claim 5, wherein the resin is selected from the group consisting of novolak resins and epoxy resins.

7. Process in accordance with claim 1, wherein the developer includes a material selected from the group consisting of dyes and pigments which is deposited on the nonlight-struck areas during development to render said areas more visible.

8. A process as claimed in claim 1, wherein the developer includes a photodesensitizing dye which is deposited on the nonlight-struck areas during development to render said areas insensitive to light.

9. Process according to claim 1, wherein said support is metal.

10. Process according to claim 1, wherein a tough nonphotosensitive layer is interposed between the photosensitive material and the support, said nonphotosensitive layer being soluble in the developer.

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