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3,454,398

METHOD OF FORMING A LITHOGRAPHIC PLATE BY TREATING SILVER HALIDE WITH A TERMINAL ETHYNYL COMPOUND TO FORM AN INK RECEPTIVE IMAGE AREA

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No Drawing. Filed Aug. 29, 1966, Ser. No. 575,564

Int. Cl. G03f 7/10; B41m 5/00

U.S. Cl. 96—33

10 Claims

This invention relates to lithographic printing, and more particularly concerns the provision of a lithographic printing plate from a photographic element. Otherwise stated, the invention concerns the conversion of a silver halide photographic image to an oleophilic, or oil-receptive, lithographic printing plate.

In the art of photolithography, a photographic image is converted into a medium that is receptive to oily or greasy inks. Desired objectives of methods for effecting this conversion include: a method which is simple, rapid, convenient, and low in cost; reagents which are readily prepared and are stable and consistent in use; lithographic printing plates which may be stored for long periods, either wet or dry, and in the presence of comparatively strong light; and a method which permits a positive printing plate to be made directly from a photographic negative.

In accordance with the invention, I have now discovered that silver halide photographic elements, or layers, may be converted to lithographic plates of outstanding quality by contacting the elements with a terminal ethynyl compound, that is, an organic compound having at least one terminal acetylenyl group. The process of the invention converts silver halide to an oleophilic ink-receptive medium, and in all respects meets the desired objectives above.

As normally employed, the reagents of the invention are applied to a negative silver halide photographic element which has been developed by the action of a convention developer, or reducing agent. Developing converts exposed portions of silver halide to metallic silver, which is not reactive with the ethynyl reagent, while retaining unexposed silver halide in the element. In this case, the developed element is not fixed.

Alternatively, a printing plate may be prepared directly from a positive photographic image. For this embodiment the emulsion is developed to convert exposed or the non-exposed parts of the silver halide to metallic silver, and is then fixed with sodium thiosulfate or a similar compound to dissolve the unexposed silver halide. After fixing, the metallic silver remaining in the element is converted to a silver halide by the action of an oxidizing agent such as cupric chloride or chromic chloride, and is then contacted with the inventive ethynyl reagent. In still another version of the invention a diffusion transfer positive may be converted to silver chloride which may then be processed according to the invention.

The reagents of the invention may be used with any of the silver halide photographic elements, and work quite well with conventional lithographic elements. The halide is preferably silver chloride, and may contain amounts of silver bromide or iodide. As will be apparent from the examples below, the silver halide-gelatin emulsion

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may be applied onto a photographic paper or onto a water-proof medium such as a polyethylene coated paper base or any transparent, translucent or nontransparent film material. These waterproof bases are usually subbed or otherwise treated to make them accept an aqueous emulsion, as known in the art.

Treatment of the developed photographic element with a terminal ethynyl compound of the invention is conveniently effected in an aqueous alkaline medium. Reagent concentrations on the order of 1:5,000 to 1:20,000 appear optimal, with concentration higher than about 1:1,000 occasionally failing to produce good prints, while concentrations below 1:50,000 being somewhat too dilute for rapid reaction. The alkali concentration does not appear to be a significant variable, and may range from less than 0.1% to more than about 4% sodium or potassium hydroxide.

The ethynyl reagent may include wetting agents such as the non-ionic detergents, hardening agents such as sodium sulfate, water soluble polymers, and other materials found useful for maintaining a clean print background.

A wide variety of ethynyl compounds may be used for the invention, and it is indeed surprising that only the presence of a terminal ethynyl group is necessary to convert a silver halide photographic element into a medium that is receptive to greasy lithographic printing inks. An unusual feature of the invention is that the remaining portion of the ethynyl molecule need not itself be oleophilic, as shown by the suitability of such ethynyl compounds as propargylalcohol and dipropargylamine.

The ethynyl compounds are readily available, and many are described in the literature. A convenient preparation is by reaction of sodium or lithium acetylene with halogen compounds (e.g., lithium acetylene converts 2-chlorobenzothiazole to 2-ethynylbenzothiazole), as is the reaction of acetylenic amines with reactive chloro compounds (e.g., the reaction of propargyl amines with cyanuric chloride). Another convenient preparation is by reaction of propargylbromide or homologous compounds with alcohols, mercaptans, and selenols (see U.S. Patent 2,769,010) to give compounds of the structure R-(halogen)-CR₂-(acetynyl), where the R groups are preferably hydrogen or organic radicals.

The ethynyl reactants advantageously but not necessarily have a cyclic group in the molecule, e.g., oxazole, thiazole, imidazole, triazine, pyrimidine, urazil, phenyl, etc. However the simpler compounds having a hydrocarbyl, alcohol, amine, or acid group are quite suitable. Further, compounds with more than two ethynyl groups are also effective, and in some instances a mixture of two or more ethynyl reagents provides exceptional results.

The ethynyl reactants of the invention are advantageously shipped and stored either as the solid products, the solid products mixed with an anhydrous alkali such as sodium or potassium hydroxide, or an aqueous solution either with or without the alkali. Alkalis however are helpful in dissolving the ethynyl compounds. Wetting agents, hardening agents, water soluble polymers, and other materials may, if desired, be included with the reactants.

The invention and various aspects thereof are exemplified in the following operating examples, which are intended to be illustrative of the invention without necessarily being exclusive or wholly definitive thereof.

EXAMPLE I

In this example a silver chloride photographic element is converted to a lithographic printing plate by the action of 2-(2-propynylthio)-ethoxy-benzimidazole.

An unwashed contrasty silver chloride emulsion is coated on an ordinary photographic paper base to a coating weight of 5.8 grams of liquid emulsion per square foot. The silver content of the emulsion is equivalent to 30 grams silver nitrate per liter, and the emulsion has a gelatin to silver nitrate ratio of 2.8. The element is hardened with glyoxal, and is incubated after coating for 65 hours at 50° C.

The element is exposed in the usual manner.

After exposure, the element is developed for 15 seconds at 25° C. with a conventional reducing agent (Eastman Kodak Developer D72, diluted with two parts of water). The paper is rinsed for 15 seconds in water at 35° C. After rinsing, the paper is immersed for 30 seconds in an aqueous alkaline solution of 2-(2-propynylthio)-ethoxy-benzimidazole, prepared as follows:

One hundred milligram of 2-(2-propynylthio)-ethoxy-benzimidazole is dissolved in 20 cc. of methanol. To this solution a still-hot solution of 30 grams sodium hydroxide in 75 cc. water is rapidly added with stirring, and the volume brought to 1500 cc. with water at room temperature.

After immersion the paper is washed in water, installed in a commercial lithographic printing press, as known in the art, and used for printing.

EXAMPLE II

In this example a lithographic printing plate is made from a photographic element by contacting the emulsion with dipropargylamine.

The emulsion is prepared in the manner of Example I, but is washed to a conductivity of 0.00800 ohms⁻¹ cm.⁻¹, then sensitized for green light, and coated on a polyethylene-coated paper base. The element is hardened with a solution of two milliliters of 37% formaldehyde per liter, and is suitable for use within a few days after coating. The element is sufficiently fast to permit it to be used in a reproduction camera.

After exposure, the emulsion is developed with a reducing agent (Eastman Kodak Developer D72, but with a reduced KBr content). The use of a waterproof polyethylene base permits elimination of a water rinsing step after developing.

The undeveloped silver chloride is converted into an ink receptive image by contacting it with an aqueous dipropargylamine solution at a concentration of 1:10,000 in 2% sodium hydroxide.

In lieu of a final rinse in plain water as in Example I, the paper is washed with an acid phosphate solution. It is dried with warm air, and produces excellent prints even after retaining it in full light for a week before use.

EXAMPLE III

Using embodiments similar to those of Examples I and II, or both, the following ethynyl compounds were used to convert silver chloride photographic elements into lithographic printing plates. In each instance similar or equivalent results to those obtained in Examples I and II were obtained:

- (1) 2-(2-propynylthio)-benzoxazole
- (2) 2-(2-propynyloxy)-benzothiazole
- (3) 2-(2-propynylthio)-benzothiazole
- (4) 2-(2-propynylthio)-benzimidazole
- (5) 2-(2-propynylthio)-5,6-dimethyl benzimidazole
- (6) 2-(2-propynylthio)-chlorobenzimidazole
- (7) 2-(2-propynylthiomethyl)-5,6-dimethyl benzimidazole
- (8) 2-(2-propynylthio)-ethylthiobenzimidazole
- (9) 2-methyl benzothiazole-propynylbromide (quaternary addition product)

- (10) 2-(2-propynylthio)-5-phenylbenzoxazole
- (11) 4,6-bis(propynylthio)-2-amino-s-triazole
- (12) 4,6-bis(propynylthio)-2-ethylamino-s-triazine
- (13) 4,6-bis(propynylthio)-2-phenylamino-s-triazine
- (14) 4,6-bis(propynylthio)-2-(methylthiophenyl) amino-s-triazine
- (15) 4,6-bis-(3,5-dimethyl-1-hexyne-3-)thio)-2-amino-s-triazine
- (16) 2-(2-propynylthio)-4-hydroxy-6-phenyl pyrimidine
- (17) 2-(2-propynylthio)-3-allyl-5,6-dimethyl-4-oxo dihydropyrimidine
- (18) 2-(2-propynylthio)-4-hydroxy-6-amino pyrimidine
- (19) The 2-propynylthio imidazole derived from 1,3-dimethyl-5,6-diaminourazole
- (20) propargylalcohol
- (21) propargylamine
- (22) propargylaniline
- (23) Reaction products of propargylamine with halogenated compounds, e.g., cyanuric chlorides, dichloro cyanuric acid, 2-chloro-4,6-diamino-2,4,6-triazine, 2-phenyl-4,6-dichloro-s-triazine
- (24) di(propargylamino) cyanuric acid
- (25) 2-propargylthio-4-amino cyanuric acid
- (26) ethyloctynole
- (27) 3-phenyl-1-butyne-3-ol
- (28) ethynylbenzene
- (29) 2-(2-propynylthiomethyl)-benzimidazole
- (30) 2-(2-propynylthio)-azabenzimidazole
- (31) 3,5-dimethylhyxyne-3-ol
- (32) 2-ethynylbenzothiazole

While the invention has been illustrated by various embodiments thereof, it is evident that many alternatives, modifications, and variations will be apparent to those skilled in the art in light of the foregoing description. Accordingly, it is intended to embrace all such alternatives, modifications and variations which fall within the spirit and broad scope of the appended claims.

I claim as my invention:

1. A method of forming a lithographic printing plate from a silver halide photographic element having exposed and unexposed portions, which comprises: developing said element to convert silver halide in said exposed portions to metallic silver, and contacting said element with a terminal ethynyl compound to convert silver halide in said unexposed portions to an oleophilic ink-receptive medium.
2. Method of claim 1 wherein said halide is chloride.
3. Method of claim 1 wherein said terminal ethynyl compound is an aqueous alkaline solution.
4. A method of forming a lithographic printing plate from a silver halide photographic element having exposed and unexposed portions, which comprises: developing said element to convert silver halide in said exposed portions to metallic silver, fixing said emulsion to dissolve silver halide from said undeveloped portions, oxidizing said metallic silver to silver halide, and contacting said element with a terminal ethynyl compound to convert silver halide remaining in said element to an oleophilic ink-receptive medium.
5. Method of claim 4 wherein said halide is chloride.
6. Method of claim 4 wherein said terminal ethynyl compound is an aqueous alkaline solution.
7. A method of forming a lithographic printing plate from an element having portions containing silver halide and portions free of silver halide which comprises: contacting said element with a terminal ethynyl compound to convert said silver halide to an oleophilic ink-receptive medium.
8. A lithographic printing plate comprising an imaged silver halide photographic element treated with a terminal ethynyl compound in an amount sufficient to render said silver halide receptive to greasy inks.

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9. Printing plate of claim 8 wherein said halide is chloride.
10. Printing plate of claim 8 wherein said terminal ethynyl compound is an aqueous alkaline solution.

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U.S. Cl. X.R.

96—29; 101—466