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PHOTOGRAPHIC PROCESS

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5 Claims. (Cl. 96—48)

This invention relates to a photographic process, and more particularly to one in which the image is completely developed by action of light, and is then fixed by the evaporation of a volatile component of the photosensitive material.

An object of the invention is to provide a photographic process which produces finished prints without chemical manipulation. The process is extremely simple. It is very flexible in that images may be obtained in a variety of colors on paper, cloth and film. Dimensional stability of paper prints is good. Other advantages will appear from the following description.

The process employs a photosensitive system comprising at least two components both of which are necessary for the photochemical reaction, and one of which is volatile, that is has a boiling point at a pressure of 760 mm. of mercury of less than 325° C. The process consists in printing out a fully formed image upon a suitably sensitized paper, cloth, or other material, and fixing the image by evaporation of the volatile component.

Co-pending application Serial No. 194,017, now Patent Number 2,676,887, issued April 27, 1954, of which the present application is a continuation-in-part discloses a photosensitive system consisting of a basic dye cyanide and an organic photoactivator, which may be volatile. Many of the photosensitive materials described in the co-pending application may be used in the presently described process.

For the present process materials sensitized with hydrophobic dye cyanides are satisfactory. Examples of suitable hydrophobic dye cyanides are the cyanides of crystal violet, malachite green, rosaniline, pararosaniline, brilliant green, and similar dyes. On the other hand, cyanides which contain hydrophilic groups, such as quaternary ammonium, and sulfonic acid, should not be employed to sensitize the materials used in the present process. Thus paper sensitized with the cyanide of methyl green, which would contain a quaternary ammonium group, would not be suitable.

Any photoactivator may be employed if it is sufficiently volatile. Examples of suitable activators are, acetonitrile, valeronitrile, capronitrile, aniline, monomethylaniline, phenylmethyl carbinol, benzyl alcohol, beta-phenylethyl alcohol, veratrole, ethylene glycol diethyl ether, tetraethylene glycol dimethyl ether. In addition to activators disclosed in the co-pending application, previously known activators, such as ethyl alcohol and acetic acid, may be used. However, for practical speed in fixing the image, the relatively non-volatile activators are less desirable. Thus ethyl and butyl phosphates are satisfactory activators for materials used in the present process, but the ortho and meta cresyl phosphates, while excellent activators, are less suitable because of their low volatility. The activator used in the present process should preferably boil below 325° C. at a pressure of 760 mm. of mercury.

Because the activated dye cyanides are sensitive only to ultraviolet radiation, printing should be carried out by direct sunlight, an ultraviolet cored carbon arc, a quartz mercury lamp, sunlamp, or other source of radiations shorter than 3300 A. U. Any printing frame glass that may be used, and the film, tracing cloth, paper or other support for the master copy from which the print is made, should transmit some radiation shorter than 3300 A. U. Commercial products suitable for printing frame glasses are Vitaglass, Corex D, Corex A, Corning glass No. 7910, fuzed quartz etc. Ordinary photographic film is quite suitable for the master copy support, as are most of the commercially available tracing cloths.

Printing is carried out until the image has the desired depth of color. The image from a negative master copy is a positive. The image is fully formed in printing and no operation of chemical development is employed.

Fixing is carried out in darkness or light free from the ultraviolet radiation to which the materials are sensitive, and consists in evaporation of the activator. A variety of methods may be employed, such as:

(1) Hanging the print at room temperature in free air.

(2) Blowing a stream of air over the print at room temperature.

(3) Blowing a stream of warm air over the print.

(4) Heating the print above the boiling point of the activator.

Method 1 is always applicable and requires normally only an hour or two with paper prints when the activator has a boiling point of up to 210° C. Method 2 also is always applicable and is faster than 1. Methods 3 and 4 are still faster, but the temperatures employed should be adapted to the material being fixed. Generally it is desirable to use temperatures that are not higher than about 100° C. to avoid heat induced decompositions. Even 100° C. may at times be too high a temperature because, for example, a film containing a low boiling activator might be blistered by the vapor formed rapidly and trapped in the film.

Fixing is complete when the activator has been removed. Adequacy of fixing can be determined by a brief test exposure of a portion of the print to ultraviolet radiation. When no color develops on such exposure fixing is adequate. However, removal of the activator can often be judged by odor or appearance of the print. Of course only volatile activators should be present in the photosensitive material. If a non-volatile activator is present as an impurity in the volatile activator, paper, film, or other materials employed, fixing will not be complete.

The following examples will illustrate the process more clearly.

Example 1

Water leaf paper is sensitized by moistening with a ½ of 1% solution of crystal violet cyanide in resorcinol dimethyl ether, and squeezing the moist paper between glass rollers to remove excess solution. The paper is printed by an S4 sunlamp through a Corex D printing frame glass and a drawing in India ink on tracing cloth until a sufficiently strong violet image (negative of the drawing) has been formed. The print is fixed by blowing on it a stream of air heated to 100° until the odor of the resorcinol dimethyl ether has disappeared, and an exposure of a portion of the print to direct sunlight for 1 minute produces no appreciable image.

Example 2

Water leaf paper is sensitized by dipping in a ¼ of 1% solution of pararosaniline cyanide in acetonitrile, and the excess solution removed by blotting with a fresh

piece of paper. The sensitized paper is printed immediately by sunlight in a frame equipped with a Vitaglass glass. A silver photographic negative on safety film is used as the master copy. Between the negative and the sensitized paper is placed a film of thin clear colorless cellophane to protect the negative from possible damage by diffusion of the acetonitrile. Behind the sensitized paper is placed a sheet of thin aluminum foil to prevent evaporation of acetonitrile during printing. When the image has been printed to sufficient depth, the print is fixed by hanging in free air at room temperature for about ten minutes.

Example 3

Paper sensitized and printed as in Example 2 is fixed by heating to 100° for 1 minute in a constant temperature oven.

Example 4

Water leaf paper is sensitized by dipping in a saturated solution (at 25° C.) of malachite green cyanide in a mixture of 1% acetic acid and 99% ethyl alcohol. Excess solution is blotted off the paper and the paper printed immediately after sensitizing behind an aluminum foil stencil in a printing frame equipped with a Corning 7910 glass and a sheet of aluminum foil behind the paper to prevent evaporation of the alcohol. Printing is by the radiation from a quartz mercury lamp until the green image is sufficiently strong. The print is fixed by exposure for 1 minute to a stream of air heated to 100° C.

Example 5

The images formed on the sensitized water leaf papers tend to "run," i. e. to diffuse laterally in the paper, and thus to give a soft focus effect to the print even when the negative is sharp. For some purposes this effect is desirable, but not for the reproduction of fine lines or print. Sharper images are obtained by the use of sized papers. A rosin sized paper is sensitized by brushing with a fresh ½ of 1% solution of crystal violet cyanide in benzyl alcohol. (At low temperatures the dye cyanide may crystallize from old solutions of this concentration.) Printing is carried out immediately after sensitization behind an India ink drawing on tracing cloth, and the image is fixed by exposure of the print for a few minutes to a stream of air heated to 100° C.

Example 6

Starch sized paper is sensitized by brushing with a solution of crystal violet cyanide saturated at 16° C. in phenylmethyl carbinol. The paper is printed behind a master copy printed in black ink on "Winston Extra Thin" tracing paper. The print is fixed by blowing a stream of air on it at room temperature.

I claim:

1. A photographic process comprising the steps of printing out an image by ultraviolet radiation upon material sensitized with a hydrophobic amino triphenylmethane dye cyanide activated by an organic activator boiling below 325° C. at a pressure of 760 mm. of mercury selected from the group consisting of veratrole, resorcinol dimethyl ether, an ethylene glycol ether, a phosphoric acid ester of a monohydroxy compound, an aromatic amine containing a hydrogen atom on the nitrogen atom, a nitrile in which the cyano group is attached to a carbon atom which also holds a hydrogen atom, an aromatic carbinol and a lower aliphatic alcohol and fixing the image by blowing a stream of air over the print until the activator is completely removed.

2. The process of claim 1 in which the air is heated.

3. The process of claim 1 in which the activator boils below 100° C. and is evaporated by blowing a stream of air over the print at a temperature above the boiling point of said activator but not in excess of about 100° C.

4. A photographic process comprising the steps of printing out an image by ultraviolet radiation upon material sensitized with a hydrophobic amino triphenylmethane dye cyanide activated by an organic activator boiling below 325° C. at a pressure of 760 mm. of mercury selected from the group consisting of veratrole, resorcinol dimethyl ether, an ethylene glycol ether, a phosphoric acid ester of a monohydroxy compound, an aromatic amine containing a hydrogen atom on the nitrogen atom, a nitrile in which the cyano group is attached to a carbon atom which also holds a hydrogen atom, an aromatic carbinol, and a lower aliphatic alcohol; and fixing the image by heating the print above the boiling point of said activator until the activator is completely evaporated.

5. The process of claim 4 in which the activator boils below 100° C. and the print is heated above the boiling point of said activator but not in excess of 100° C.

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