

1

3,236,648

PHOTOGRAPHIC PROCESS FOR FORMING VISIBLE DYE CYANIDE IMAGES

Lyman Chalkley, Prince Georges County, Md.

(5320 Middleton Lane, Washington 22, D.C.)

No Drawing. Filed Dec. 24, 1962, Ser. No. 246,674
12 Claims. (Cl. 96—48)

This invention relates to a photographic process, and more particularly to one in which photosensitive material is activated by heat during the photographic exposure.

This application is a continuation-in-part of my application Serial Number 752,535, now U.S. Patent Number 3,071,464, applied for on August 1, 1958.

Photographic methods have many advantages for the duplication of documents, recording of data and storage of information. The operations of development and fixing associated with photographic methods are disadvantages, and various devices have been introduced to reduce the burden of these operations.

From the standpoint of convenience the ideal process would be one in which neither development nor fixing would be required. This goal is approached by the direct printing out processes in which the image is completely formed by the action of light alone without need for supplementary development of any sort to bring out the image.

However, the printing out processes have their own limitations. They require more exposure to produce an image than a good developing out process. Therefore, printing speed may become a problem and it is desirable to use as fast printing material as possible. Also the unexposed portions of a print that has not been developed or fixed retain their sensitivity and are further printed when exposed to actinic radiation with the result that the print becomes fogged when examined, copied or otherwise used in an illuminated place. The effect of fogging can be materially reduced by the use of printing out photographic materials that are sensitive only to ultraviolet radiation, because prints made upon them can be examined or copied by visible light, and even projected upon a screen, without fogging. However, few visible light sources are completely free of ultraviolet, and some, such as fluorescent lamps, are relatively rich in ultraviolet. Therefore fogging remains more or less of a problem, especially with printing out materials having the greatest printing speed.

The present invention provides an additional means for reducing the fogging of prints made upon printing out materials, while retaining maximum printing speed. While the process of Serial Number 752,535 was based upon the utilization of photosensitive naphthalene derivatives that had an inherent high temperature coefficient for their photochemical reactions, the present process is based upon the difference in photosensitivity of activated dye cyanide materials when the activator is in a state of fusion and when it has solidified.

Thus the photographic materials for the present process employ the triarylacetonitrile derivatives commonly known as dye cyanides, preferably hydrophobic dye cyanides, and fusible activators that will be in their solid state at temperatures at which the exposed prints are to be used and stored, while being capable of fusion at higher temperatures at which the actual printing will be carried out.

2

In such systems the photosensitivity is much, often a hundred times or more, greater when the activator is in a state of fusion than when it is solid.

The photographic process consists in heating the photosensitive material to a temperature above the fusion point of the activator employed, exposing the material while the activator is liquid to actinic radiation to the production of a visible color or image and cooling the print to a temperature at which the activator solidifies.

The means for heating the photosensitive material for its exposure is in no way critical so long as the activator is in a state of fusion during exposure. The methods for heating described in copending application Serial Number 752,535 may be employed. Other simultaneous heating and exposure mechanisms are equally satisfactory. Thus a very useful way of carrying out the process is in commercial blue print and diazo print machines that employ a hot mercury lamp. These machines will heat the photographic material by the heat from the lamp, often to temperatures of 90° C. or more, and produce excellent prints on materials used in the present process.

The process is useful for copying documents, for duplicating purposes such as printing from a stencil, for recording mirror galvanometer traces, for other recording instruments such as barographs, pyrometers, etc., for printing from photographic negatives and the like. The process has the advantages that it is fast, requires no chemical processing by either gasses or liquids, prints out the full image instantly without physical or chemical development and provides prints that develop little or no fog on use at ordinary temperatures although additional material may be printed upon them at any later time by raising the temperature. The present process is not limited to materials sensitized with photosensitive naphthalene derivatives as in the process of Serial Number 752,535 although it may use such material and so combine the advantages of both of the processes. Other unique advantages will appear from the following discussion.

Fusible activators for use in the process may be drawn from known classes of photoactivators for dye cyanides, such as carboxylic acid amides, phosphoric acid esters, carboxylic acids, primary and secondary amines, polyoxy compounds, nitriles containing a hydrogen atom on the carbon atom next to the nitrile group, aromatic carbinols. Other fusible activators may be used.

The temperature at which the activator fuses is related to the conditions under which the printed photographic materials are to be employed. Under arctic conditions the activator might fuse at as low a temperature as 0° C., or even lower. In temperate zones an activator that fuses between 35° and 150° C. may be used. The fusion point does not have to be sharp, and fusion may take place over a number of degrees.

The solid phase of the activator may be crystalline, but it is not necessary for the success of the process that it be crystalline. Thus the solid succino nitrile exists in both a crystalline and an amorphous form, and succino nitrile is a good fusible activator for the process. What is necessary is that the activator shall, within the range of temperatures used in the process, be capable of existing in both a solid form and a fused liquid form.

Examples of fusible activators that have been found suitable for use in the process are: succino nitrile, stearonitrile, stearamide, propionamide, N-methyl acetanilide,

triphenyl phosphate, tri-p-cresyl phosphate, diphenylamine, N,N'-diphenyl-ethylenediamine, p-methoxyphenol, n-butyl-p-hydroxybenzoate, 4-phenoxy-butyronitrile, alpha-phenoxy-propionic acid.

Because of solubility relationships the simple dye cyanides that do not contain ionized salt groups are generally most useful in the process. Among these the hydrophobic dye cyanides and the dye cyanides containing hydroxyl groups are satisfactory. Examples of suitable dye cyanides are the cyanides of p-Rosaniline, Rosaniline, New Fuchsin, Malachite Green, Setoglaurine, Crystal Violet, Victoria Blue B, Victoria Blue 4R, Hexa-B-hydroxy-ethyl-p-Rosaniline.

The process is based upon the phenomenon that fusible activators for dye cyanides vary enormously in their activating power between their solid and liquid states. A fusible activator is one that possesses both a rigid solid state and a liquid fused state separated by a temperature difference. Such substances melt when heated and may, when pure, have sharp melting points although they may, especially in commercial mixtures, melt over a considerable range of temperature. They are distinguished by their melting behavior from plastic and colloidal activators such as gelatine, polyvinyl alcohol, cellulose, nylon and other plastic polymers. However, a crystalloidal fusible polymer may act as a fusible activator if it has photoactivating power at all for dye cyanides. The most generally useful fusible activators are organic materials. In a fused activator a dye cyanide usually prints more than 100 times as fast as in the same activator when the latter has solidified. Activators may be mixed with each other so long as the mixture is fusible. The dye cyanide should be separated in sensitized materials from non-fusible activators that would impart sensitivity at all temperatures.

The following examples illustrate basic principles and simple forms of the process.

Example 1

Into 100 g. of molten p-methoxyphenol at 65° C. is stirred 0.1 g. of finely powdered Crystal Violet cyanide, which dissolves readily. The resulting solution is divided equally between two identical shallow glass dishes. The two dishes are placed side by side, but one is cooled to 25° C. with complete solidification of its contents and the other is placed on a hot plate that maintains its temperature at 60° C. and its contents liquid. In the dark both samples remain colorless.

The surfaces of the p-methoxyphenol solutions are exposed simultaneously to the same amount of radiation from a 20 watt fluorescent sunlamp placed 10 inches above the dishes for 5 minutes. The liquid will then have taken on a strong violet color while the solid in the dish at 25° C. will have developed at most a slight gray or blue tint. Analysis of the two samples shows that the amount of Crystal Violet dye in the mixture that had been molten during the exposure is more than 100 times the amount of Crystal Violet that is present in the mixture that was solid during the exposure.

Example 2

Into 100 g. of molten succino nitrile at 60° C. is stirred and dissolved 1 g. of Malachite Green cyanide. The solution is poured onto a flat aluminum plate that is being whirled at 60 r.p.m. while heated to 65° C. When the solution is evenly distributed the coated plate is transferred to a cake of ice to solidify the succino nitrile to a waxy film that covers the metal surface. The colorless solid film is little sensitive to radiation and the coated plate may be stored indefinitely before printing if evaporation of the succino nitrile is prevented.

To print upon this plate it is placed on a horizontal hot plate at 60 to 70° C. whereupon the succino nitrile melts and forms a liquid film that has over 100 times the printing speed of the solid succino nitrile film. Printing is effected by a strong beam of ultra violet radiation of wave

lengths shorter than 3300 Å. The green image prints out immediately and printing is terminated by cutting off the ultra violet beam when the image has reached a desired density. The image is fixed by immediate transfer of the aluminum plate to a cake of ice to chill it and solidify the succino nitrile film. The chilling and solidification of the activator stops diffusion of the printed out dye in the liquid film and reduces the sensitivity to radiation to less than 1% of its value when the film was liquid. The print is permanent so long as it is not heated above the fusion point of the activator and is protected from abrasion and evaporation of the succino nitrile.

Example 3

An absorbent water leaf paper, such as filter paper, is impregnated by dipping in a solution of 1 g. of p-Rosaniline cyanide and 100 g. of commercial stearamide melting at about 97-100° C., in a mixture of 150 ml. of acetonitrile and 150 ml. of toluene at 65° C. The moist paper is dried in a stream of air heated to 110° C. to remove the solvent acetonitrile and toluene mixture. The sensitized paper may then be stored indefinitely at room temperature.

To print upon it, the paper is heated in an oven, on a hot plate or by any of the devices shown in copending application Serial Number 752,535 to 110° C. and while at this temperature exposed to radiation of wave length shorter than 3250 Å. until a magenta image prints out. The exposure is then terminated and the paper removed from the heating device to chill in the ambient air to room temperature and so fix the image. The printing speed of this paper when the photoactivator is in its liquid phase is over 200 times the printing speed when the photoactivator is solid.

Samples of the p-Rosaniline cyanide and stearamide paper have been stored unexposed in the dark at room temperature for over five years without deterioration or loss of sensitivity, while exposed prints have been stored an equal time without loss of the image.

Example 4

Water leaf paper is impregnated with a solution of 1 g. of Setoglaurine cyanide and 50 g. of tri-p-cresylphosphate in 400 ml. of toluene, dried in air heated to 120° C. and stored at room temperature. Printing is done by heating the paper to 90° C., exposing it while the tri-p-cresyl phosphate is molten and chilling to below 50° C. to fix the print.

Example 5

Absorbent paper is impregnated with a solution of 1 g. of Victoria Blue B cyanide and 50 g. of N-methylacetanilide in 500 ml. of toluene, dried from toluene in a stream of air heated to 100° C. and stored at room temperature. Printing is done by heating the paper to 110° C. and exposing it to wave lengths shorter than 3700 Å. while the N-methylacetanilide is molten and then chilling it to room temperature to fix the print.

Since Victoria Blue B cyanide is one of the high temperature coefficient derivatives of a diphenyl-naphthylmethane dye the use of this sensitizer combines the advantages of the process of copending application Serial Number 752,535 with those of the fusible activator process.

Example 6

The sensitized impregnated papers work well in the process but they do not give as high resolution as a coated paper and when used in a printing frame in contact with a drawing or master copy may transfer some color to the master copy. For such uses dry surface coated papers are preferable. These may be prepared by application of a dispersion of the dye cyanide and fusible activator in a film forming material to a sized paper.

For example, 1 g. of Crystal Violet cyanide is dissolved in 50 g. of molten N-ethylacetanilide a 65° C., and this

solution is poured slowly with violent stirring into 1500 ml. of 10% aqueous gelatine solution, also at 65° C., containing 5 g. of an emulsifying agent such as triethanol ammonium stearate. Stirring is continued until a homogeneous milky emulsion is obtained of the N-ethylacetanilide solution in the gelatine solution.

The emulsion is then coated at 50° to 65° C. onto a sized paper such as is used to sensitize with diazo compounds, the paper chilled to set the gelatine and dried.

The paper is printed by heating above 55° C., exposing to light of wave length shorter than 3250 Å. while the N-ethylacetanilide is molten and then chilling to room temperature to fix the print. The dry gelatine serves as an effective barrier between the emulsified particles of molten activator and both the supporting sheet of paper and any drawing, negative or master copy against which the sensitized paper may be pressed while printing.

Materials suitable for use in the process may be prepared in a variety of other forms such as sensitized films and plates and fabrics, and suitable sensitized coatings may be applied in other ways, as by letter press and lithographic press. The coatings themselves may have other formulations and may employ a variety of vehicles to carry the dye cyanide and fusible activator mixture. Many other suitable dye cyanide and fusible activator photosensitized materials will be apparent to those skilled in the art.

In addition to the printing apparatus illustrated in co-pending application Serial Number 752,535 numerous commercial machines are suitable for carrying out the process. The heat from the lamps of large diazo paper printing machines raises the temperature of the paper being printed sufficiently to provide very satisfactory printing on dye cyanide and fusible activator sensitized papers and foils. Examples of such machines are the Pease "Pacemaker," Bruning "Copyflex" and Paragon-Revolute printers. Only the printing sections of these machines are used because there is no need for processing of the prints by either vapors or liquids. Exposure of the printed papers to the ambient atmosphere chills them sufficiently to solidify the activator and thus fix the image. Other types of commercial machines that can be used for the process are the presses equipped to print with heat set inks. While the paper is heated by the hot cylinder or oven, any sensitized areas or impressions on the paper may be printed by an auxiliary ultra violet lamp with a stripe or spot marker or other design. The print is fixed by chilling on the following chilled rolls.

The use of other commercial apparatus and design of new machines for carrying out the process will be apparent to those skilled in the art.

I claim:

1. The photographic process comprising the steps of raising the temperature of a photosensitive material containing fusible activator and a dye cyanide that is isolated from infusible activators to above the fusion point of the activator, exposing said material to light while the activator is in a state of fusion to form a visible color and then chilling the colored material to a temperature at which the activator solidifies.

2. The photographic process comprising the steps of raising the temperature of a photosensitive material containing fusible organic activator intimately mixed with a dye cyanide that is isolated from infusible activators to above the fusion point of the activator, exposing said material to light while the activator is in a state of fusion to form a visible color and then chilling the colored material to a temperature at which the activator solidifies.

3. The photographic process comprising the steps of raising the temperature of a photosensitive material containing organic activator that fuses in the temperature range of 35° to 150° C. intimately mixed with a dye cyanide that is isolated from infusible activators to above the fusion point of the activator, exposing said material to light while the activator is in a state of fusion to form

a visible color and then chilling the colored material to a temperature at which the activator solidifies.

4. The photographic process comprising the steps of raising the temperature of a photosensitive material containing fusible organic activator intimately mixed with a hydrophobic dye cyanide that is isolated from infusible activators to above the fusion point of the activator, exposing said material to light while the activator is in a state of fusion to form a visible color and then chilling the colored material to a temperature at which the activator solidifies.

5. The photographic process comprising the steps of raising the temperature of a photosensitive material containing organic activator that fuses in the temperature range of 35° to 150° C. intimately mixed with a hydrophobic dye cyanide that is isolated from infusible activators to above the fusion point of the activator, exposing said material to light while the activator is in a state of fusion to form a visible color and then chilling the colored material to a temperature at which the activator solidifies.

6. The photographic process comprising the steps of raising the temperature of a photographic sheet material photosensitized with a dye cyanide that is isolated from infusible activators but intimately mixed with a fusible activator for the same to above the fusion point of the activator, exposing said photographic sheet to light while the activator is in a state of fusion to form a visible image and then chilling the printed sheet to a temperature at which the activator solidifies.

7. The photographic process comprising the steps of raising the temperature of a porous sheet, which does not itself photoactivate the dye cyanide employed, impregnated with a photosensitive mixture of dye cyanide and fusible organic activator for the dye cyanide to above the fusion point of the activator, exposing the said sheet to light while the activator is in a state of fusion to print a visible image and then chilling the printed sheet to a temperature at which the activator solidifies.

8. The photographic process comprising the steps of raising the temperature of a porous sheet, which does not itself photoactivate the dye cyanide employed, impregnated with a photosensitive mixture of a hydrophobic dye cyanide with fusible organic activator for the dye cyanide to above the fusion point of the activator, exposing the said sheet to light while the activator is in a state of fusion to print a visible image and then chilling the printed sheet to a temperature at which the activator solidifies.

9. The photographic process comprising the steps of raising the temperature of a porous sheet, which does not itself photoactivate the dye cyanide employed, impregnated with a photosensitive mixture of a hydrophobic dye cyanide with organic activator that fuses in the temperature range of 35° to 150° C. to above the fusion point of the activator, exposing the sheet to light while the activator is in a state of fusion to print a visible image and then chilling the printed sheet to a temperature at which the activator solidifies.

10. The photographic process comprising the steps of raising the temperature of a sheet carrying on its surface a layer photosensitized with a mixture of fusible organic activator and a dye cyanide that is isolated from infusible activators to above the fusion point of the activator, exposing the said sheet to light while the activator is in a state of fusion to print a visible image and then chilling the printed sheet to a temperature at which the activator solidifies.

11. The photographic process comprising the steps of raising the temperature of a sheet carrying on its surface a layer photosensitized with a mixture of fusible organic activator and a hydrophobic dye cyanide that is isolated from infusible activators to above the fusion point of the activator, exposing the said sheet to light while the activator is in a state of fusion to print a visible image and then chilling the printed sheet to a temperature at which the activator solidifies.

12. The photographic process comprising the steps of raising the temperature of a sheet carrying on its surface a layer photosensitized with a mixture of organic activator that fuses in the temperature range of 35° to 150° C. and a hydrophobic dye cyanide that is isolated from infusible activators to above the fusion point of the activator, exposing the sheet to light while the activator is in a state of fusion to print a visible image and then chilling the printed sheet to a temperature at which the activator solidifies.

References Cited by the Examiner**UNITED STATES PATENTS**

2,936,235	5/1960	Chalkley	-----	96—90
2,951,855	9/1960	Chalkley	-----	96—90
3,071,464	1/1963	Chalkley	-----	96—27

NORMAN G. TORCHIN, *Primary Examiner.*A. LIBERMAN, *Assistant Examiner.*