

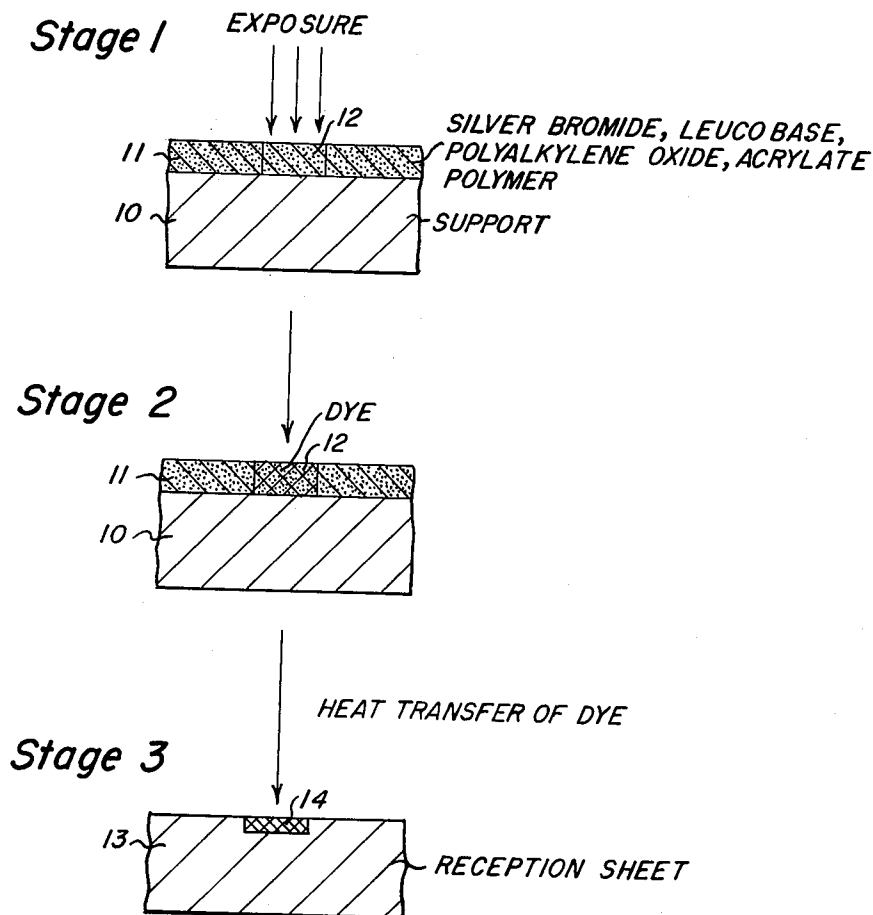
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PHOTOGRAPHIC PROCESSES UTILIZING PHOTOLYTIC HALOGEN

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PHOTOGRAPHIC PROCESSES UTILIZING PHOTOLYTIC HALOGEN

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3 Claims. (Cl. 96—29)

This invention relates to photographic processes utilizing photolytic halogen to bring about the formation, and more particularly, the thermographic transfer of a colored image.

The invention involves exposing imagewise a layer containing a compound which releases photolytic halogen upon exposure to light, in the presence of a substance changing color upon oxidation by the halogen.

One embodiment of the invention includes exposing a photographic silver halide emulsion layer so as to release a photolytic halogen imagewise and using the resultant halogen through an oxidation reaction, to produce a visible image.

In a search for a practical photographic reproduction process utilizing photolytic halogen (e.g. halogen released upon exposure of silver halide to light) for the formation of a colored image, it was found that photolytic halogen was capable of effecting an imagewise change in color of a layer of dye such as fluorescein. This was demonstrated by exposure of a film having a layer of silver bromide, in contact with a sheet impregnated with fluorescein dye with the result that as the bromine was released from the silver bromide in the region of exposure, it diffused to the fluorescein dye layer and oxidized the dye to a purple image. When the dye was replaced with other compositions which responded with a color change on oxidation, such as starch-iodide, a similar result was obtained.

In a similar manner, it was found that a silver bromide emulsion layer could be exposed to an image in the presence of a leuco base with the result that the photolytic bromine released from the silver bromide oxidized the leuco base to the dye. This was demonstrated in one case by coating a gelatino-silver bromide emulsion containing leuco Malachite Green on a cellulose ester surface, such as paper coated with cellulose ester, followed by wetting the emulsion layer and exposing it to a subject for a time sufficient to yield photolytic bromine imagewise which oxidized the leuco base to the dye. Upon removal of the emulsion with warm water, a green dye image was found on the cellulose ester surface. A magenta image was obtained in a similar manner by use of leuco Pararosaniline.

A preferred process of our invention utilizing photolytic bromine and leuco bases of dyes, embodies a light-sensitive element comprising a hydrophilic organic colloid layer containing silver halide, leuco base and polymeric materials adapted to control the formation of the photolytic halogen image. Upon oxidation of the leuco base by the photolytic halogen the resultant dye image is transferred to a reception layer by thermographic means.

The accompanying drawing shows in greatly enlarged cross-sectional view a representative sensitive element useful in the preferred process of the invention and the various stages of the process of obtaining a photographic reproduction therefrom.

In this preferred process of the invention, a dispersion of silver bromide in a hydrophilic organic colloid such as gum arabic is exposed imagewise in the presence of a polyalkylene oxide such as Carbowax 4000 and in the presence of a soft acrylate polymer dispersion and a leuco base. The photolytic halogen generated by exposure of

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the silver bromide to light oxidizes the leuco base to a dye. When the exposed layer is heated in contact with a reception sheet, the dye image dissolved in the polyalkylene oxide transfers imagewise to the sheet yielding a negative reproduction of the subject.

The following examples will serve to illustrate our invention.

Example 1

The following composition was prepared. To 5 cc. of a 25 percent aqueous dispersion of 90 percent polyethylacrylate and 10 percent polyacrylonitrile was first added with stirring 10 cc. of water followed by 10 cc. of an emulsion prepared by adding 50 cc. of 1 N silver nitrate and 50 cc. of 1 N potassium bromide to 60 cc. of 2 percent aqueous gum arabic solution. Thereafter 5 cc. of a 30 percent aqueous solution of Carbowax 4000 (polyethylene oxide of approximate molecular weight 4000) and 2 cc. of a 3.3 percent solution of leuco Malachite Green in ethyl alcohol was added. The resulting composition was coated upon a paper support which had previously been rendered water-resistant by coating with a cellulose ester. The resultant sensitive element is shown in stage 1 of the drawings wherein layer 10 represents the support carrying the sensitive layer 11 prepared as described above. After drying the sensitive element was exposed in area 12 under a line negative for 20 seconds using a photoflood lamp at a distance of 8 inches. A green dye image appeared in the exposed area 12 as shown in stage 2 of the drawing. The exposed layer was then placed in contact with a paper reception sheet and the sandwich heated for 2 seconds at approximately 80° C. Upon separation of the two sheets, it was found that a portion of the green dye image had transferred to the paper to provide a sharp image of the subject shown in stage 3 wherein layer 13 represents the paper reception sheet and image 14 the green dye image which had transferred thereto. The stability of this dye print was tested by exposing it to a high intensity light source which resulted in the background areas remaining white indicating that in the transfer step no silver halide had transferred.

In the above process the leuco base may be replaced by other leuco bases such as leuco Pararosaniline, leuco Auramine, etc. The Carbowax 4000 may be replaced by similar amounts of other polyalkylene oxides such as polypropylene oxide and polybutylene oxides. The lower molecular weight polyalkylene oxides containing an average of from about 35 to 100 alkoxy units in the polymer chain, are best suited to the process since they more readily facilitate transfer of the dye image to the reception sheet.

The acrylic polymers of the sensitive element may be prepared in a well-known manner by polymerization in water of alkyl acrylates such as methylacrylate, ethylacrylate, methylmethacrylate in the presence of a dispersing agent alone or together with other acrylic monomers including acrylonitrile so as to obtain hydrosol dispersions of the soft, water insoluble acrylate polymers suited to the process.

Another photographic reproduction process utilizing photolytic halogen for effecting a color change in contiguous oxidizable substances is as follows:

Example 2

The following elements were provided:

A. A film carrying an internal latent image silver halide emulsion such as described in Davey et al. U.S. Patent 2,592,250.

B. A photographic paper base which had been dipped in an aqueous solution containing 5 percent soluble starch and 1 percent potassium iodide.

Coating A was soaked for 30 seconds in distilled water and held in contact with B in a photographic printing

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frame with the emulsion in contact with the starch layer while exposure was made by a photoflood lamp 8 inches above a line positive.

After separating of the elements, a purplish image was formed which is characteristic of the color of the starch iodine complex. The exposure produced photolytic halogen which oxidized the potassium iodide producing iodine which reacted with the starch to form the color.

Example 3

A water resistant paper base was coated with the following composition:

0.1 g. [1,1'-diethyl-4,4'-carbocyanine iodide] dissolved in 10 cc. methyl alcohol added to 40 cc. 3 percent aqueous photographic gelatin solution containing 1 percent potassium iodide.

The coated paper was used in the process of Example 2 in place of film B with the result that the image produced in this experiment was cyan in color and positive by virtue of dye bleaching in the areas in which photolytic halogen oxidized the potassium iodide to iodine.

Example 4

Two films were provided as follows:

A. A film such as film A of Example 2.

B. A film carrying a fine-grain silver chloride emulsion.

Coating B was fogged by exposing it for 4 seconds to a photoflood lamp at a distance of 8 inches.

Coatings A and B were each immersed in distilled water for 30 seconds and placed together as described in Example 2 and exposed in like manner.

After separating A and B, coating B was placed for 1 minute in a conventional silver halide developing solution, rinsed in running water and fixed. A positive image of high density and very low background was obtained in film B. The photolytic halogen formed in the exposed areas had removed the latent image from the fogged silver chloride emulsion.

Example 5

The use in the invention of an organic compound releasing halogen upon exposure to light is illustrated by this example. The following elements were provided:

A. 0.1 g. of leuco Malachite Green in 10 ml. of ethyl alcohol and 0.05 g. of 2-iodo-1,3-diphenyl-1,3-propanedione in 10 ml. ethyl alcohol were added to 50 ml. of 4

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percent aqueous gelatin solution and the final solution coated upon a water resistant paper support at a coverage of 5.6 ml. per sq. ft.

B. Same as A but the iodo compound omitted.

Elements A and B were exposed 20 seconds to a photoflood lamp at 6 inches through a line subject. A green image was obtained only in A. When the gelatin layer of A thus exposed was removed with warm water a green image remained in the support.

10 What we claim is:

1. A photographic process which comprises exposing to a subject a supported layer of a mixture of, a soft water-insoluble acrylate polymer of the class consisting of alkyl acrylate and alkyl methacrylate polymers, a polyalkylene oxide, a leuco base of a triphenylmethane dye soluble in said polyalkylene oxide and silver bromide, until an appreciable amount of photolytic bromine has been released from the exposed silver bromide and has oxidized the leuco base to a dye in the region of exposure, heating the layer in contact with a reception sheet to transfer at least a portion of the dye imagewise from the layer to the sheet.

2. The process of claim 1 wherein the transfer of dye imagewise from the layer to the reception sheet is followed by heating the layer in contact with another reception sheet to transfer a further portion of the dye imagewise to the sheet.

3. The process of claim 1 wherein the polyalkylene oxide is polyethylene oxide.

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