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METHOD OF PRODUCING DYE IMAGES

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This invention relates to a method for producing colored photographic images and particularly to a method of forming colored images in the bleach-out process of color photography.

The first application of the bleach-out process of color photography was described by Christensen U. S. Patent 1,517,049, November 25, 1924. As is now well known, the Christensen process consisted in producing a colored image by bleaching a dyed gelatin layer containing a silver image in a solution of a strong reducing agent such as sodium hydrosulfite or stannous chloride, to decolorize the dye in the regions of the silver image. The Christensen process made use of water-soluble polyazo dyes as image forming dyes.

In Seymour U. S. Patent 2,184,022, December 19, 1939, a somewhat similar but improved process was described in which vat dyes were used in place of azo dyes and sodium stannite was employed in place of stannous chloride as a bleach bath. It was found that better bleaching could be accomplished by the use of sodium stannite than by the use of the stannous chloride or the sodium hydrosulfite of Christensen, especially with vat dyes.

When the sodium stannite treatment of the Seymour U. S. Patent 2,184,022 was extended to the treatment of polyazo dyes it was found that many such dyes bleached only slightly when treated with sodium stannite in the presence of a silver photographic image. Means, accordingly, were sought to increase the bleaching action on numerous polyazo dyes.

It is, therefore, the principal object of the present invention to provide a method for bleaching a polyazo dye in the region of a silver photographic image with a sodium stannite bleach bath. A further object is to produce a photographic image formed of a polyazo dye by bleaching portions of the dye in the region of a silver image. Other objects will appear from the following description of our invention.

These objects are accomplished by exposing, developing and fixing a photographic layer containing a polyazo dye uniformly dispersed therein, and then soaking the layer in a dilute solution of a strong acid prior to bleaching the dye selectively in an alkaline stannous chloride bleach bath.

The photographic element treated according to our invention may comprise a single emulsion layer or a plurality of emulsion layers coated on one or both sides of a suitable support. The support may be transparent material such as glass, cellulose ester or synthetic resin or an opaque material such as a pigmented cellulose ester or paper. The emulsion layer or layers may contain a uniformly dispersed dye prior to

exposure and also may contain a dye intermediate from which a colored compound may be formed, after exposure. If a three-layer photographic element is used for the production of natural color images, the three emulsion layers preferably contain dyes each of which is roughly complementary in color to the effective sensitivity of the emulsion layer in which it is coated. It will be understood that in the normal arrangement of the layers, such as that described in the Christensen Patent 1,517,049, the outer layer is blue-sensitive and colored yellow, the middle layer is green-sensitive and colored magenta and the layer nearest the support is red-sensitive and colored blue-green. The yellow image-forming dye in the outer emulsion layer absorbs the blue light which otherwise would fog the middle and inner emulsion layers. As further protection a separate filter dye may be incorporated in the outer emulsion layer or in a filter layer located between the outer and middle emulsion layers.

The essential feature of our invention is the treatment of the photographic layer with a dilute aqueous solution of a strong acid after fixing and before bleaching. Usually this treatment does not destroy the dye in the layer but in the case of dyes difficult to bleach with sodium stannite, we have found that the layer treated in this way can be more readily bleached by sodium stannite than without such treatment. Strong acids suitable for this treatment include hydrochloric, nitric and sulfuric acids. A preferred bath is one made by mixing 10 cc. of concentrated sulfuric acid with enough water to make one liter of solution. By "strong acid" we mean an acid which is highly ionized, usually to an extent of about 70% or more when mixed with water. It will be readily understood that many strong acids are not highly ionized in concentrated solution but are more nearly completely ionized in dilute solution. We include within the scope of our invention the use of organic as well as inorganic strong acids.

The method of processing a photographic layer according to our invention will now be described.

A photographic layer is exposed in a suitable manner such as under a color separation image or under a natural color transparency in the case of a multi-layer element. The element is then developed for about 8 minutes at 68° F. in a solution of the following developer:

55 Monomethyl-p-aminophenol sulfate	grams	2
Hydroquinone	do.	5
Sodium sulfite (dessicated)	do.	100
Borax (granular)	do.	20
60 Water to	liters	1

The print is then placed for 2 minutes in a stop bath which may have the following composition:

Acetic acid (28%)	cc.	500
Water	liters	4

The element is then thoroughly fixed in acid hypo of the following composition:

Water (about 125° F.)	cc.	600
Sodium thiosulfate	grams	240
Sodium sulfite (dessicated)	do.	15
Acetic acid (28%)	cc.	48
Boric acid crystals	grams	7.5
Potassium alum	do.	15
Water	liters	1

The element is again washed and is then treated for 16 minutes in an acid bath of the following composition:

Sulfuric acid (concentrated)	cc.	10
Water to	liter	1

After the treatment in the acid bath, the element is placed immediately in a suitable bleaching solution such as one having the following composition:

Stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$)	grams	15
Water to	cc.	500
Sodium hydroxide (6% solution)	do.	500

This bath destroys the dye or dyes selectively in the region of the silver image.

After a wash the silver image is oxidized in a bath having the following composition:

Cupric chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$)	grams	100
Hydrochloric acid (concentrated)	cc.	25
Water to	liter	1

The silver salt thus formed is removed by fixing in a fixing solution such as that described above.

The dyes which may be used to form the photographic image or images according to our invention include the cyan dye, Pontamine East Green 5BL (du Pont), the magenta dye made by tetrazotizing 4,4'-diamino-3,3',6,6'-tetramethyltriphenylmethane and coupling it with heptoyl H acid, and the cyan dye made by diazotizing p-amino-N-methylacetanilide, and coupling the product with ethoxy Cleve's acid (1,6) and then diazotizing this product and coupling it with N(4''-amino-4'-benzoyl amino benzoyl) gamma acid.

The emulsion layers in the case of a multi-layer element need not be colored complementary to their sensitivity but may be colored with a dye that transmits the color for which the layer in which it is incorporated is mainly sensitive. Layers colored in this way obviously do not produce a natural color image directly.

Other modifications of the invention will be apparent to those skilled in the art and it is to be understood that our invention is to be taken as limited only by the scope of the appended claims.

We claim:

1. The method of forming a colored image in a photographic layer containing a bleachable polyazo dye uniformly dispersed therein and a silver image, which comprises treating the layer in a dilute solution of a strong acid, and then bleaching the dye in the region of the silver

image in an alkaline stannous chloride bleach bath.

2. The method of forming a colored image in a photographic layer containing a bleachable polyazo dye and unexposed silver halide uniformly dispersed therein, which comprises exposing and developing said layer, removing the undeveloped silver halide without affecting the silver image formed by development, treating the layer in a dilute solution of a strong acid and then bleaching the dye in the region of said image in an alkaline stannous chloride bleach bath to form a colorless compound and leave unaffected the dye in the remaining portions of the layer.

3. The method of forming a colored image in a photographic layer containing a bleachable polyazo dye and unexposed silver halide uniformly dispersed therein, which comprises exposing and developing said layer, removing the undeveloped silver halide without affecting the silver image formed by development, treating the layer in a dilute solution of sulfuric acid and then bleaching the dye in the region of said image in an alkaline stannous chloride bleach bath to form a colorless compound and leave unaffected the dye in the remaining portions of the layer.

4. The method of forming a colored image in a photographic layer containing a bleachable polyazo dye and unexposed silver halide uniformly dispersed therein, which comprises exposing and developing said layer, removing the undeveloped silver halide without affecting the silver image formed by development, treating the layer in a dilute solution of hydrochloric acid and then bleaching the dye in the region of said image in an alkaline stannous chloride bleach bath to form a colorless compound and leave unaffected the dye in the remaining portions of the layer.

5. The method of forming a colored image in a photographic layer containing a bleachable polyazo dye and unexposed silver halide uniformly dispersed therein, which comprises exposing and developing said layer, removing the undeveloped silver halide without affecting the silver image formed by development, treating the layer in a dilute solution of nitric acid and then bleaching the dye in the region of said image in an alkaline stannous chloride bleach bath to form a colorless compound and leave unaffected the dye in the remaining portions of the layer.

6. In the method of forming a colored photographic image by bleaching a polyazo dye in the region of a silver photographic image with alkaline stannous chloride, the step which comprises treating the dye containing layer prior to bleaching with a dilute solution of a strong acid.

7. In the method of forming a colored photographic image by bleaching a polyazo dye in the region of a silver photographic image with alkaline stannous chloride the step which comprises treating the dye containing layer prior to bleaching with a dilute solution of sulfuric acid.

8. In the method of forming a colored photographic image by bleaching a polyazo dye in the region of a silver image, the steps which comprise treating a layer containing said dye and silver image with a dilute solution of a strong acid and then bleaching the dye in the region of the silver image with an alkaline stannous chloride solution.

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