

UNITED STATES PATENT OFFICE

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DYE BLEACHING PROCESS

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4 Claims. (Cl. 95—6)

This invention relates to color photography and particularly to a bleaching method of forming dye images.

It is well known that in the dye bleaching method of color photography in which a dye uniformly dispersed in a photographic emulsion layer is bleached in the region of a silver image, a positive image is produced when the layer is exposed to a positive scene or image. According to the usual procedure a silver halide layer containing the dye from which the image is produced is exposed to a positive and developed to a negative silver image. The layer is then fixed and the dye bleached in the region of the negative silver. This leaves a positive dye image.

It is frequently desirable to produce a negative print or transparency by the dye bleaching method when printing from a color positive or a positive color print or transparency when printing from a color negative. To produce such print or transparency of color aspect opposite to the original, by the usual dye bleaching method, it is necessary to resort to a reversal process. According to this process the negative silver produced upon first development must be first removed and this step alone is frequently difficult since the image forming dye must not be destroyed in the operation. It is then necessary to convert the residual silver halide to metallic silver to form the agent which determines the bleaching of the dye. This procedure requires a great number of steps and introduces difficulties in the choice of baths suitable for removal of the silver.

It is therefore an object of the present invention to provide a dye bleaching process of color photography in which a negative color image is produced from a positive original or a positive color image is produced from a negative color original. A further object is to provide a method for the production of a natural color positive image by the dye bleach method.

These objects are accomplished by exposing a silver halide layer containing a uniform dispersion of an image-forming dye, developing it, removing the metallic silver and bleaching the dye in the regions of the residual silver halide. This method avoids the separate step of converting the residual silver halide to metallic silver to form the agent which determines the regions in which the dye is bleached.

My process is applicable to multi-layer films as well as single layer films and is particularly suitable for making prints from motion picture color separation negatives with silver images or

from color negatives consisting of dye images. For example, a film exposed to a color negative or successively to color separation negatives through suitable filters is processed by the following steps.

1. Develop
2. Treat in acid stop bath
3. Wash
4. Remove first-developed silver with potassium bichromate and sulfuric acid
5. Wash
6. Treat in sodium bisulfite solution
7. Wash
8. Bleach dye with sodium stannite.
9. Clear with sodium citrate and citric acid
10. Remove silver with potassium bichromate and sulfuric acid or cupric chloride followed by hypo
11. Wash

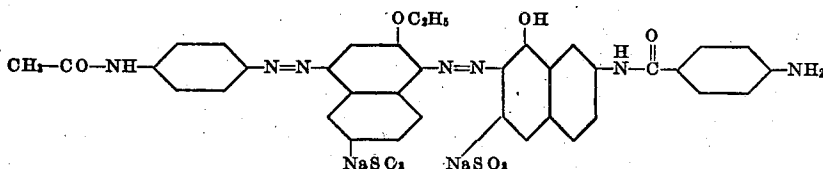
One of the features essential to the operation of my process is a method for bleaching the dye in the presence of silver halide rather than metallic silver. A method for accomplishing this bleaching of the dye is described in the copending application of Ehrenfried, Serial No. 360,622, filed October 10, 1940. According to the method described in that application, certain azo dyes may be bleached in the region of a silver halide image by treatment in sodium stannite. During the bleaching operation the silver halide is converted to metallic silver and the silver formed in this way must be removed at the end of the bleaching operation in order to produce a clear and transparent dye image. This removal of the silver, however, adds no additional steps to the normal process, since silver bleaching and fixing steps are necessary even in the case of bleaching in the presence of metallic silver.

The following example illustrates a multi-layer film which is suitable for processing according to my invention.

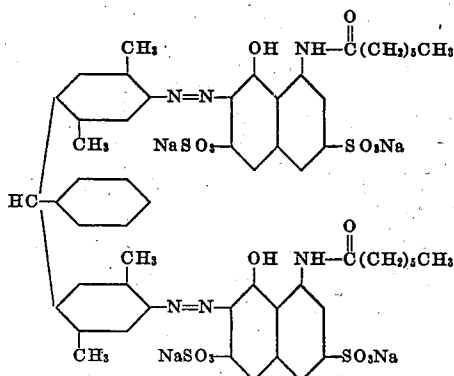
On a support of cellulose ester, glass, paper, synthetic resin or other suitable material, there are coated gelatino silver halide layers sensitive respectively to the red, green and blue regions of the spectrum. The red-sensitive layer is normally coated next to the support and the blue-sensitive layer outermost. Between the blue-sensitive and green-sensitive layers there is preferably coated a yellow filter layer such as a removable dye or a layer of colloidal silver.

The red-sensitive layer has incorporated therein a cyan dye made by diazotizing p-aminoacetanilide and coupling it in acid solution with

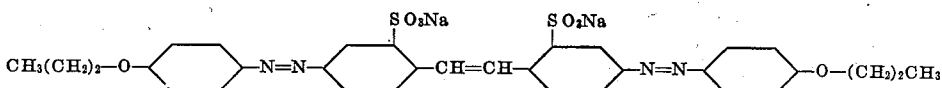
ethoxy Cleve's beta acid (1-naphthylamine-2-ethoxy-6-sulfonic acid), again diazotizing and coupling in alkaline solution with p-aminobenzoyl gamma acid 2(p-aminobenzoylamino) 8-naphthol-6-sulfonic acid. This dye has the following structural formula:



The green-sensitive layer is colored with the dye formed by diazotizing 4,4'-diamino-3,3',6,6'-tetramethyltriphenylmethane and coupling it in alkaline solution with two moles of heptoyl H acid (1-heptoyl amino-8-naphthol-3,6-disulfonic acid). This dye has the following structure:

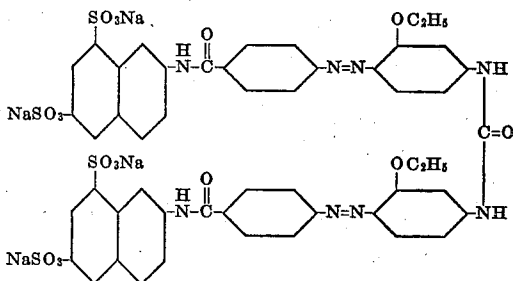


The unsensitized layer is colored with the dye made by tetrazotizing 4,4'-diaminostilbene-2,2'-disulfonic acid and coupling it in alkaline solution with two moles of phenol and forming the di-n-propyl ether of the product. This dye has the following structure:



An alternative dye for the unsensitized layer is the following:

The dye formed by diazotizing 2(p-aminobenzoylamino) naphthalene-6,8-disulfonic acid, coupling it in acid solution with m-phenetidine, and treating the resulting product with phosgene to form the urea dye. This dye has the following structure:



An alternative dye for the red sensitive layer is the following:

The cyan dye formed by diazotizing metanilic acid, coupling it in acid solution with 1-naphthylamine-7-sulfonic acid, diazotizing and coupling in acid solution with ethoxy Cleve's (1,6) acid (1-naphthylamine-2-ethoxy-6-sulfonic acid), and

coupling in alkaline solution with the product of the reaction of diazotized metanilic acid coupled in acid solution with J acid (2-amino-5-naphthol-7-sulfonic acid).

The following processing procedure is suitable for the multi-layer element described above.

15 After exposure, the element is developed in the following solution:

p-Monomethyl-aminophenol sulfate	grams	1
Sodium sulfite (desiccated)	do	75
Hydroquinone	do	9
Sodium carbonate (desiccated)	do	25
Potassium bromide	do	5
Ammonium thiocyanate	do	1
Water to	liter	1

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The element is then treated in a stop bath containing 33 cc. per liter glacial acetic acid, washed and the silver is removed in the following bath:

30 Potassium bichromate	grams	2.5
Sulfuric acid	cc	5
Water to	liter	1

The element is then treated in 200 grams per liter sodium bisulfite solution and washed. The dye is then bleached in the region of the residual silver halide by treatment for about five minutes in the following bath:

40 Stannous chloride	grams	40
Sodium hydroxide	do	46
Triethanolamine	cc	50
Water to	liter	1

50 The silver is then bleached to silver halide in the following bath:

Cupric chloride	grams	100
Hydrochloric acid	cc	25
Water to	liter	1

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This is followed immediately by the following silver halide removal bath:

Hypo	grams	240
Sodium sulfite (desiccated)	do	15
60 Acetic acid (28%)	cc	48
Sodium metaborate	grams	15
Potassium alum	do	15
Water to	liter	1

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With certain image-forming dyes it is sometimes advantageous to treat the element in a clearing bath before and after the dye bleach. A clearing bath of the following composition used for five minutes before bleaching in order to remove calcium salts which affected bleaching of certain dyes is suitable:

Sodium benzoate	grams	1.2
Sodium citrate	do	30
75 Citric acid	do	20
Water to	liter	1

The following clearing bath used for fifteen minutes after bleaching removes reduction products of certain dyes and prevents their reoxidation to produce stain.

Sodium citrate	grams	30	5
Sodium sulfite	do	30	
Citric acid	do	20	
Water to	liter	1	

My invention is susceptible of the modifications falling within the scope of the appended claims.

I claim:

1. The method of producing a reversed dye image in a photographic silver halide layer containing a uniform dispersion of an azo dye, which comprises exposing said layer, developing a silver image therein, removing said silver image without affecting the residual silver halide, and then bleaching the dye in the region of the residual silver halide in a bleach bath comprising a stannite of an alkali metal.

2. The method of producing a positive dye image in a photographic silver halide layer containing a uniform dispersion of an azo dye, which comprises exposing said layer to a negative image, developing a silver image therein, removing

said silver image without affecting the residual silver halide, and then bleaching the dye in the region of the residual silver halide in a bleach bath comprising a stannite of an alkali metal.

3. The method of producing a positive dye image in a photographic silver halide layer containing a uniform dispersion of an azo dye, which comprises exposing said layer to a negative image, developing a silver image therein, removing said silver image in an acid bichromate bath without affecting the residual silver halide, and then bleaching the dye in the region of the residual silver halide in a bleach bath comprising a stannite of an alkali metal.

4. The method of forming a natural-color photographic image in a multi-layer element having at least one gelatino-silver halide layer containing a uniform dispersion of an azo dye, which comprises exposing said element to a color negative, developing a silver image therein, removing said silver images without affecting the residual silver halide, and then bleaching the dye in the regions of the residual silver halide in a bleach bath comprising a stannite of an alkali metal.

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