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METHOD OF PRODUCING COMBINED COLORED AND BLACK AND WHITE PICTURES

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8 Claims. (Cl. 95—2)

The present invention relates to a method for the production of an additional black and white or dark metallic silver image in a photographic material in which dyestuffs or dyestuff-forming substances for the formation of the colored image are present in the layer. It has been found that very good dyestuff pictures combined with a black and white silver image can be obtained if the formation or the destruction of the dyestuff is effected in such a manner that the remaining silver halide is not fixed and, if, for the formation of colored pictures, there are used substances which do not dissolve the silver halide or destroy its light sensitivity.

The special technical advantage of this method lies in the fact that in the production of the additional silver image it is not necessary to rely on the selective sensitivity of the individual or partial layers. This process is particularly suitable for the production of sound films in which the dyestuff picture can be combined with a black silver image for emphasizing the deep blacks or shadows.

A further advantage of this method is that it is possible to produce perfectly clear black and white sound records because the dyestuff may be entirely destroyed in the sound area of the film.

This process is equally suitable for photographic materials in which the dyestuff-forming substances or the dyestuffs are initially present in the layer or in which these substances are brought into the photographic layer after exposure.

Example 1

A picture is printed on an ordinary light sensitive positive film. The film is developed, but not fixed, and is then soaked with a solution, for instance, of an azo-dyestuff, such as Chicago Blue (Schultz Farbstofftabellen VII Ed. No. 511) or with a dyestuff-forming substance such, for instance, as the leuco-ester of thioindigo pink (Schultz, l. c. No. 1353). The films dyed in this way are further treated for the destruction of the dyestuff or the formation of the dyestuff, as shown in the following example. A further picture is printed after the formation of the dyestuff image and is developed and then the whole film is fixed.

Example 2

A photographic three-color material such, for instance, as is described in my prior British Patents Nos. 408,991 (U. S. Patent No. 1,985,344) or 415,040 (U. S. application Ser. No. 642,960, filed November 16, 1932) and comprising three light sensitive layers I, II and III colored blue-green, yellow and purple respectively with, for instance, Diamine Pure Blue (Schultz l. c. No. 510), Chrysophenin G (Schultz l. c. No. 726) and Diamine Fast Pink (Ullman, Encyclopädie der Technischen Chemie II Ed. Vol. 3, pg. 647) respectively is taken. Layer I is predominantly sensitized for green and is coated direct on to the support. Layer II is predominantly sensitized for red and is coated on to the other side of the support and layer III is an ordinary blue sensitive silver halide emulsion and is coated on top of layer II. Three partial images are printed from positive master images into this material and are developed in the usual way but not fixed. The area of the sound record, however, is diffusely exposed in all layers, whereby homogeneous silver deposits are produced in all of the layers. The destruction of the dyestuffs is then effected with a solution of an indifferent acid, as, for instance, a 2% solution of hydrobromic acid in which the dyestuff is locally destroyed proportionate to the silver image. Then the metallic silver is re-halogenized, for instance, with:—

(*a*) A solution of 0.25 gm. potassium bichromate and 10 gr. hydrochloric acid per litre of water, or

(*b*) Cupric bromide; or

(*c*) 2 gm. of potassium ferricyanide and 10 gm. of bromide of potassium in 200 gm. of water.

It is then washed, clarified with sodium bisulphite and dried in the dark. The sound record and, if desired, a black and white key print, are then printed from negative master images of the sound record and the key print respectively. Then the film is developed a second time and finally fixed. The result is a three-color image with a superimposed black key print and with a black and white sound record.

For the same purpose a material may also be used which, in addition to colored layers, also contains a colorless silver halide emulsion layer. Layers which contain dyestuff-forming substances, as indicated for instance in U. S. Patent No. 1,956,017, patented April 24, 1934, or in British Patents Nos. 416,566 (U. S. Patent No. 2,071,688) and 416,660, may also be used if, after the first development, the formation or destruction of the dyestuff is performed by such chemical means as do not dissolve the silver halide or do not remove its light sensitivity, for example, dyestuff formation may be effected by bromic acid and dyestuff destruction by a 2% solution of hydrobromic acid.

Example 3

Photographic layers which contain the leuco-ester of vat dyestuffs are exposed and developed and the dyestuff is formed by treatment with a solution containing one per thousand potassium bichromate and one per thousand hydrobromic acid. The silver image is at the same time re-halogenized. The dyestuff image is then clarified by sodium sulphite solution, washed and dried in the dark and then again, as above stated, exposed, developed and fixed. The result is a dyestuff picture which is combined with a black and white image.

I claim:—

1. A method of producing photographic and kinematographic pictures which comprises exposing a light sensitive silver halide layer, developing the latent silver image to form a metallic silver image, incorporating in said layer a color substance selected from the group consisting of dyestuffs and dyestuff-forming substances which may be locally reacted under the influence of said silver image to form a final dyestuff image, treating said layer with an agent which reacts with said silver to form some silver halide and an agent which acts in situ upon said color substance to form a dyestuff image, reconverting any remaining silver to light-sensitive silver halide by treatment with an oxidizing agent free of solvents for silver salts and which does not deleteriously affect said dyestuff image, exposing the rehalogenized layer a second time to produce a latent silver image from the silver halide, developing the last mentioned image and fixing after this second development.

2. A method of producing photographic and kinematographic pictures which comprises exposing a light sensitive silver halide emulsion layer containing a dyestuff for the formation of a dyestuff image which may be locally destroyed under the influence of a silver image, developing the latent silver image to form a metallic silver image, treating said layer with a dye-destroying agent which reacts with said silver to form some silver halide and an agent which acts in situ upon said dyestuff to form a dyestuff image, reconverting any remaining silver to light sensitive silver halide by treatment with an oxidizing agent free of solvents for silver salts and which does not deleteriously affect said dyestuff image, printing an image into the rehalogenized layer containing the dyestuff image, developing the last mentioned image to form a metallic silver image and fixing after the second development.

3. A method of producing photographic and kinematographic pictures, which comprises exposing a multi-layer photographic material including three differently colored and differently sensitized layers containing dyestuffs for the formation of a multi-color image which dyestuffs may be locally destroyed under the influence of a silver image, developing the latent silver images to form silver images, treating said layer with a dye-destroying agent which reacts with said silver to form some silver halide and an agent which acts in situ upon said dyestuffs to form dyestuff images, reconverting any remaining silver to light sensitive silver halide by treatment with an oxidizing agent free of solvents for silver salts and which does not deleteriously affect said dyestuff images, printing an image into the rehalogenized material containing the dyestuff images, developing said last mentioned image to form a metallic silver image, and fixing after said second development.

4. A method of producing combined colored and black and white photographic and kinematographic pictures which comprises exposing a multi-layer material including a plurality of differently colored and differently sensitized layers containing dyestuffs for the production of a multi-color image to positive master images, said dyestuffs being adapted to be locally destroyed under the influence of a silver image, developing the latent silver images to form silver images, destroying the dyestuffs at the points of the silver images by treatment with an agent which reacts with said silver to form some silver halide and an agent which acts in situ upon said dyestuffs to form dyestuff images, reconverting any remaining silver to light sensitive silver halide by treatment with an oxidizing agent free of solvents for silver salts and which does not deleteriously affect said dyestuff images, exposing the rehalogenized material containing the multi-color image to a negative master image to produce a latent silver image in at least one of the layers, developing the last mentioned latent silver image and fixing after this second development.

5. A method of producing combined colored and black and white photographic and kinematographic pictures which comprises exposing a multi-layer photographic material comprising a plurality of differently sensitized layers containing different dyestuff-forming substances for the production of a multi-color image to positive master images, said dyestuff forming substances being such as may be reacted under the influence of a silver image to form a dyestuff image, developing the latent silver images to form silver images, converting the dyestuff forming substances at the points free of the silver images into dyestuff images by treatment with an agent which reacts with said silver to form some silver halide and an agent which acts in situ upon said dyestuff forming substances to form dyestuff images, reconverting any remaining silver to light sensitive silver halide by treatment with an oxidizing agent free of solvents for silver salts and which does not deleteriously affect said dyestuff images, exposing the rehalogenized material containing the multi-color image to a negative master image to produce a latent silver image in at least one of the layers, developing the last mentioned latent silver image and fixing after this second development.

6. A method of producing colored kinematographic pictures having black and white sound records and black and white images which comprises exposing a photographic material including a plurality of silver halide emulsions containing dyestuffs for the production of a multi-color image and selectively sensitized to different spectral ranges, to positive master images of the colored subject, said dyestuffs being adapted to be locally destroyed under the influence of a silver image, developing the latent silver images to form metallic silver images, producing positive dyestuff images in the emulsions by treatment with a dye destroying agent which reacts with said silver to form some silver halide and an agent which acts in situ upon said dyestuffs to form dyestuff images, reconverting any remaining silver to light sensitive silver halide by treatment with an oxidizing agent free of solvents for silver salts and which does not deleteriously affect said dyestuff images, exposing the rehalogenized emulsions containing the dyestuff images

to a negative master image of the sound record and the black and white subject to produce a latent positive silver image in at least one of the emulsions, developing the last mentioned silver image and fixing after this second development.

7. A method of producing photographic and kinematographic pictures from a material including a light sensitive silver halide layer containing a developed but unfixed metallic silver image and a coloring substance selected from the group consisting of dyestuffs and dyestuff forming substances which may be locally reacted under the influence of the silver image, which comprises treating said layer with an agent which reacts with said silver to form some silver halide and an agent which acts in situ upon said coloring substance to form a dyestuff image, reconverting any remaining silver to light sensitive silver halide by treatment with an oxidizing agent free of solvents for silver salts and which does not deleteriously affect said dyestuff image, exposing the rehalogenized layer a second time to produce a latent silver image, developing the last mentioned image and fixing after the second development.

8. A method of producing photographic and kinematographic pictures from a material including a plurality of differently sensitized silver halide layers each of which contains a developed but unfixed metallic silver image and a coloring substance selected from the group consisting of dyestuffs and dyestuff forming substances which may be locally reacted under the influence of the silver image, which comprises treating said layers with an agent which reacts with said silver to form some silver halide and an agent which acts in situ upon said coloring substance to form dyestuff images, reconverting any remaining silver to light sensitive silver halide by treatment with an oxidizing agent free of solvents for silver salts and which does not deleteriously affect said dyestuff images, exposing the rehalogenized material a second time to produce a latent silver image, developing the last mentioned image and fixing after this second development.

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