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M. W. SEYMOUR

1,900,870

PHOTOGRAPHIC COLOR PROCESS

Filed April 26, 1932

Camera exposure

Fig.1.

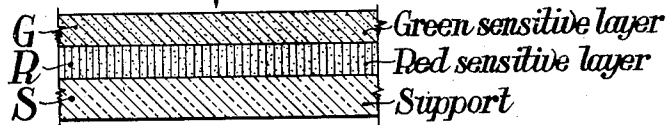


Fig.2.

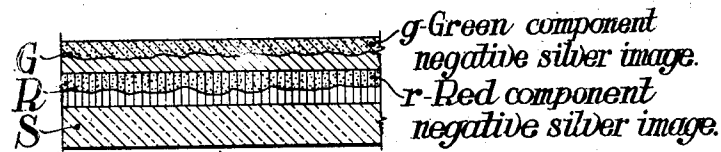


Fig.3.

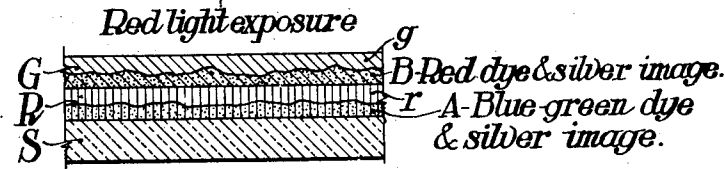


Fig.4.

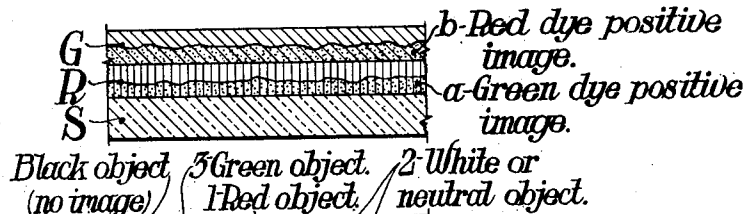


Fig.5.

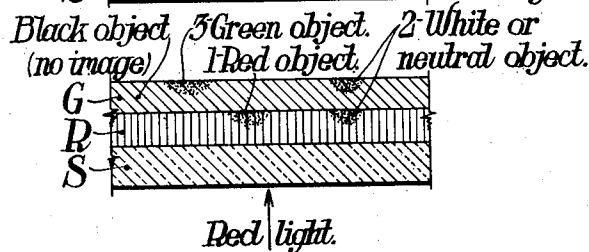
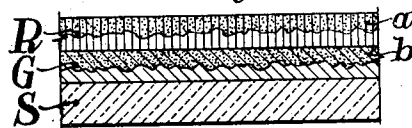


Fig.6.



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UNITED STATES PATENT OFFICE

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PHOTOGRAPHIC COLOR PROCESS

Application filed April 26, 1932. Serial No. 607,570.

This invention relates to a two-color subtractive photographic process of the type involving the use of superposed differentially color-sensitized layers. Several processes of this type have been heretofore developed involving various features in common with the process here proposed. However, the procedure outlined here is found to give improved results over those previously suggested and my invention resides in the particular combination of steps claimed, which, when used together, give particularly successful results. The process includes as necessary features the use of a material having differentially sensitized layers in which there are developed silver images, and thereafter by color development differentially colored dye and silver images, all the silver images being left in the layers until the final step when they are removed simultaneously. By this series of steps, I am enabled to obtain particularly good color separation between the layers and to simplify the process as a whole. Reference will now be made to the accompanying drawing, in the several figures of which the same characters designate the same parts. All of the figures are sectional views on an exaggerated scale of a film used in my process and showing the images in the various stages of the procedure.

Fig. 1 indicates an unexposed sensitive film.

Fig. 2 indicates the same film after exposure and the first development.

Fig. 3 indicates the film after a second exposure and development.

Fig. 4 indicates the finished product.

Fig. 5 shows on an even more exaggerated scale the position of the silver images at the step indicated in Fig. 2, and

Fig. 6 indicates the final product in a film in which the order of the layers is different than in the preferred form.

My invention may be more clearly understood from the following complete description of one embodiment.

A film support S is coated with two emulsion layers R and G in superposition. This element may be made in the manner described in my application Serial No. 559,347, filed August 25, 1931. The two layers are spe-

cifically sensitized to green and red respectively by non-diffusing sensitizing dyes. The lower layer R is sensitized for red light by a non-diffusing specific red sensitizing dye having a well-defined minimum sensitizing action in the green. Such a dye is, for example, 4, 4' diphenyl 3, 3' diethyl-7 (4-phenyl thiazole ethiodide) methyl thiazolecarbocyanine iodide. The upper layer G is specifically sensitized for green light by a green sensitizer of which 1'-2-diethyl-3,4-benzothio-pseudocyanine iodide, is a good example. Both of these dyes have the property of resisting diffusion into the adjacent layer.

A film so prepared is exposed to a colored light image in an ordinary camera or by printing from a color positive, a yellow filter being used to screen out the blue-violet portion of the spectrum to which both emulsion layers are sensitive.

The film is treated as follows: It is developed seven minutes in a motion picture positive developer such as the following:

FORMULA No. I

Water	40 liters
Monomethyl p-aminophenol sulfate	12 grams
Sodium sulfite	1600 grams
Hydroquinone	240 grams
Sodium carbonate	750 grams
Potassium bromide	36 grams
Citric acid	28 grams
Potassium metabisulfite	60 grams

The temperature is maintained at 65° F.

The film is then washed for ten minutes.

The condition of the film at this stage is indicated in Fig. 2, where there is shown in layer R a silver negative image *r*, this being the red sensation record, and in layer G a green sensation negative silver record *g*.

Without removing the developed negative silver image, the film is exposed through the support as indicated by the arrow in Fig. 2 for two seconds at one foot from a 15-watt lamp through a filter transmitting only deep red light, to which only the unexposed salts of layer R are sensitive.

It is now developed ten minutes in the fol-

lowing blue-green color-forming developer, forming a mixed silver and blue-green dye image A in layer R.

FORMULA No. II

5	Sodium carbonate, 10% solution	4 liters
	Sodium sulfite	50.0 grams
10	p-amino-diethyl-aniline hydrochloride	100.0 grams
	3.5 dibromo-o-cresol 50 g. per liter of 95% ethanol	2.0 liters
	Water to	20 liters

15 The film is again washed ten minutes.
At this point the film is fully exposed to white light and the remaining operations may be carried out in white light.

20 The film is now developed ten minutes in the following red color-forming developer, forming a mixed silver and red dye image B in layer G.

FORMULA No. III

Solution A

25	Sodium carbonate, 10% solution	8 liters
	Sodium sulfite	100 grams
	p-amino-diethyl-aniline hydrochloride	100 grams
30	Potassium bromide, 100 g. per liter	200 c. c.

Solution B

	Cyanacetophenone	100 grams
35	Ethanol 95%	4 liters
	Ethyl- α -chloroacetoacetate	200 c. c.

40 Solution A is added to solution B and the resulting mixture is made up with water to 20 liters.

The film is again washed ten minutes.

45 At this point the film contains silver images formed in all three of the developers mentioned, in addition to the two color images. These silver images are now removed by bleaching ten minutes in the following solution:

	Potassium bromide, 10% solution	1 Liter
	Potassium ferricyanide, 10% solution	1
50	Water to	10

The film is then fixed in plain hypo, 30% solution, and is finally washed ten minutes and dried.

55 The advantage of allowing the silver images to remain until the last step where two differentially sensitized layers are used will now be more particularly pointed out. The condition of the film after the completion of the first development is shown diagrammatically in the condition shown in Fig. 2, which is a much magnified cross-section of the film. The black dots in the drawing represent grains of silver developed in the non-staining developer; the masses of dots represent the

images of exposures to colored light of graduated intensity. Since the original exposure and the penetration of the developer are both from above, these images tend to lie nearer the upper surface of each emulsion layer, penetrating farthest in those areas of greatest exposure. The remaining portions in the two emulsion layers represent unexposed and undeveloped silver bromide.

70 For correct color rendering the green developer should develop all those portions of the red sensitive layer, and of this layer only, that were not developed in the first developer. Strictly speaking, none of the green sensitive layer should develop. If it were possible to find red and green sensitizing dyes which had mutually exclusive sensitizing bands which did not overlap, this condition could be realized. In practice, however, such dyes are not available and it would be usually true that the sensitizing bands of the red and green sensitizers overlap somewhat and that there is a certain amount of diffusion of the sensitizers from one layer to another in some stage of the process so that portions of the green sensitive layer may also be rendered developable by exposure to red light. This results in a certain amount of color degradation. By allowing the silver images, particularly the silver images developed in the two layers by the first or ordinary developer, to remain in the film and by exposing to red light from the support side, as done in my invention, it will be seen that the green sensitive layer is protected against the action of the red light to a considerable extent. Referring to Fig. 5, the direction of the red light exposure is that indicated by the arrow. A red sensation image 1, a green sensation image 3, and green and red sensation images constituting together a white or neutral image 2 are shown as developed in the first non-staining developer. The underlying silver of the red sensation image *r* in the red sensitive layer will screen the green sensitive layer from the action of red light. It is only in any areas unoccupied by a red sensation image that the green sensitive layer will not be protected. Thus, even if the green sensitive layer should be somewhat sensitive to red light also, as the result of diffusion of sensitizers or overlapping sensitivity bands, it will be protected against development in the green developer except in such areas as are not occupied by the red sensation image.

120 This step results in a material improvement in the differentiation of the green image, assuring reasonably satisfactory color separation. All that remains to be done after development of the green image is to expose the film fully to white light, develop the remaining silver bromide in a red color developer and remove the silver images with suitable bleaches.

It is readily seen that if the green sensitive layer should be coated next the support and the red sensitive layer above it, the same process may be carried out by applying a green light exposure through the support or the red light exposure from the emulsion side. The camera exposure would preferably be through the support. The finished positive is indicated in Fig. 6, the reference characters designating the same elements as in the other figures.

The described advantages obtained by leaving the negative silver image in the film and applying the first colored light exposure through the support are lost when the negative silver image is removed, as with a bichromate bleach prior to the second exposure.

I consider as included in my invention all modifications and equivalents coming within the scope of the appended claims.

Having now described my invention, what I claim as new and desire to secure by Letters Patent is:

1. The method of making a multi-color record that comprises exposure to a light image of an element carrying a plurality of differentially color sensitized layers, developing the affected portions to form uncolored silver images, exposing the element to light of a color capable of affecting only one of said layers, developing a silver and color image in the layer so exposed, exposing the element to white light, developing in the other of said layers a silver and color image, then removing all said silver images in the several layers in a single operation, leaving a color image in each layer.

2. The method of making a multi-color record that comprises exposure to a light image of an element carrying two differentially color sensitized layers, developing the affected portions to form uncolored silver images, exposing the element to light of a color capable of affecting only one of said layers, developing a silver and color image in the layer so exposed, exposing the element to white light, developing in the other of said layers a silver image and a color image different in color than that first developed, and then removing all four said silver images in the two layers in a single bath leaving color images of different color in the two layers.

3. The method of making a multi-color record that comprises exposure to a light image of two differentially color sensitized layers carried by a common support, developing in an ordinary developer the affected portions to form silver images, exposing the element to light of a color capable of affecting only one of said layers, developing the layer so exposed in a color developer forming also a silver image, exposing to white light, developing the other layer in a color developer yielding a silver image and also an image of a color complementary to

that formed by the first color developer, and finally removing by means of a silver solvent bleach the silver images formed by all of the developers, leaving complementary color images in the two layers.

4. The method of making a multi-color record that comprises exposure to a light image of a sensitized element comprising a support, next the support a red sensitive layer and over said red sensitive layer a green sensitive layer, developing in an ordinary developer the affected portions of both layers to form silver images, exposing the element to uniform light of a color to which only one layer is sensitive from the direction toward which said layer lies, developing said layer in a color-forming developer which also forms a silver image, exposing to uniform white light, developing in a color-forming developer which forms a silver image and also yields a color complementary to that given by the first color developer, and finally bleaching and removing all the silver images formed, leaving differently colored images in the layers.

5. The method of making a multi-color record that comprises exposure to a light image of a sensitized element comprising a support, next the support a red sensitive layer and over said red sensitive layer a green sensitive layer, developing in an ordinary developer the affected portions of both layers to form silver images, exposing the element to uniform light of a color to which only one layer is sensitive from a direction opposite to that from which the first exposure was applied, developing said layer in a developer forming a silver and a color image, exposing to uniform white light, developing in a color developer which yields a silver image and also a color complementary to that given by the first color developer, and finally bleaching and removing all of the silver images formed, leaving complementary colored images in the two layers.

6. The method of making a multi-color record that comprises exposure to a light image of a sensitized element comprising a support, next the support a red sensitive layer and over said red sensitive layer a green sensitive layer, developing in an ordinary developer the affected portions of both layers to form silver images, exposing the element from the support side to uniform red light, developing the red sensitive layer in a blue-green color developer forming also a silver image, exposing to uniform white light, developing in a red color developer forming also a silver image, and finally bleaching and removing all the silver images formed, leaving blue-green and red images in the respective layers.

7. The method of making a multi-color record that comprises exposure from the support side to a light image of a sensitized ele-

ment comprising a support, next the support
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5 tions of both layers to form silver images,
exposing the element from the emulsion side
to uniform red light, developing the red
sensitive layer in a blue-green color developer
forming also a silver image, exposing to uni-
10 form white light, developing in a red color
developer forming also a silver image, and
finally bleaching and removing all the silver
images formed, leaving red and blue-green
images in the respective layers.

15 Signed at Rochester, New York this 19th
day of April, 1932.

MERRILL WILMER SEYMOUR.

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