Nov. 11, 1941. V. B. SEASE ET AL 2,262,055

METHOD OF COLOR PHOTOGRAPHY

Filed Jan. 25, 1940

Fig. 1.

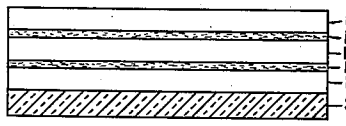


Fig. 2.

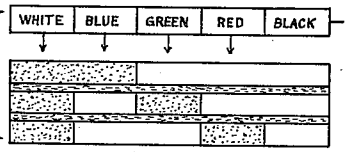


Fig. 3.



Fig. 4.



Fig. 5.



Fig. 6.

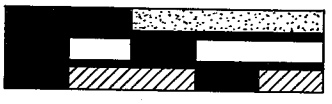


Fig. 7.



Fig. 8.

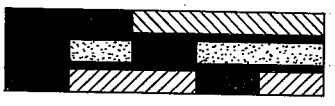
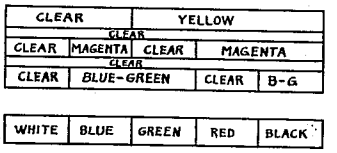


Fig. 9.



Fig. 10.



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2,262,055

METHOD OF COLOR PHOTOGRAPHY

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Application January 25, 1940, Serial No. 315,616

11 Claims. (Cl. 95—2)

This invention relates to color photography, and more particularly to the color-processing of improved photographic elements containing light-barrier layers. Still more particularly it relates to the color-processing of multilayer photographic elements which contain light barrier layers, especially multilayer film for color cinematography. It provides broadly for using the same film, for first the negative and finally the positive images and furthermore provides improved method of processing these images to duplicated color images. Another object of this invention is to provide an improved multilayer film. An additional object is to apply improved methods of processing such multilayer films to complete color films. Further objects will more plainly appear from the detailed description herein presented in illustration and not in limitation thereof.

This invention has for an object the provision of a process for developing and processing photographic elements to color photographs which involves a few simple steps. A further object is to process an exposed photographic element in a practical manner which will faithfully and accurately record a colored scene. A still further object is to provide a process of color development which enables one to satisfactorily develop the middle or buried layer of an integral mono-pack containing three differentially sensitized silver halide emulsion layers. A further object is the provision of a practical process of generating reverse dye images of proper tonal properties in multilayer film. Still other objects will appear hereinafter.

Many methods have been suggested for preparing colored photographs, but even the most improved of these, particularly those dealing with superposed multi-layer film requires such a degree of skill and control that the average photographer cannot process his own exposed films. Furthermore, the large number of steps involved in processing film by prior art methods renders the cost prohibitive to many photographers. The previous methods of color cinematography involving superposed multilayer film fall into two general classes: (1) those in which the respective photosensitized layers are uniformly colored and the color is discharged differentially with respect to the silver images formed by development, (2) those in which colors are formed step-wise and differentially in respect to the silver images formed by development. Each of these processes is quite involved and requires a great deal of handling of the film. The first-mentioned process known commonly as a "bleach-out" process, depends upon the bleaching-out or removing of dye in direct proportion to the density of the silver in the image. In actual practice it has been difficult to bleach out the dyes entirely in those areas which should be clear of dye. Variations and impurities in the dyes themselves, variations in dyes of the same name or index number but made by different manufacturers, variations in the purity of the chemicals of the bleach-bath and local variations in the rates of penetration of these baths through the multilayers, have made this process incapable of producing colored photographs on a volume basis.

The second process is even more delicate in its processing requirements since it depends on the controlled diffusion of developers, bleach-baths and stop-baths through thin layers of gelatin. Variations in coating weight, hardness of gelatin, swelling characteristics of the gelatin, temperature of baths, etc., make extremely difficult the volume production of colored photographs by this method.

This application is a continuation-in-part of our copending application, Serial No. 121,904, filed January 22, 1937 now U. S. Patent No. 2,191,502 of February 27, 1940, which is directed to novel film elements which may be processed in accordance with the teachings hereof.

The novel film constructions which may be used in accordance with this invention, when used for recording an original scene are composed of a series of photo-sensitive silver salt emulsions which are individually sensitized and so arranged that their utilizable sensitivity record the blue, green and red regions of the spectrum respectively. Silver salt layers heavily fogged during preparation are interposed between the color sensitive layers. A yellow filter layer is also embodied in the film so that the green and red layers will not be exposed to the blue region of the spectrum, e. g. blue, violet and ultra violet.

In one important embodiment of the invention the layers of the element are so arranged that light from the scene is first incident on a blue sensitive emulsion. A water-soluble, yellow filter material may be incorporated in the blue sensitive layer or in a clear colloidal layer such as a gelatin layer beneath the blue sensitive layer. Suitable materials include dyes, e. g. Luxol Fast Yellow T, Tartrazine, Naphthol Yellow, and the yellow styryl dyes of Middleton application, Ser. No. 197,310, filed March 21, 1938, etc. The light then passes through a prefogged emulsion layer, then a green sensitive emulsion layer, then a prefogged emulsion layer which contains a red dye (e. g. Carmosine M or Acid Magenta), a red sensitive emulsion layer and finally through the transparent base.

The amount of silver salt in the fogged layers, which is generally a silver halide such as silver chloride, silver bromide, silver iodide or mixtures of such halides or silver ferrocyanide and the fogging exposure given such materials, is prefer-

ably such that upon the first development of the element a light barrier will be formed in the emulsions so that less than 1% of light will be transmitted by either of them. The formation of the black barrier layers provides an effective blocking control of the printing light penetration.

In using a film of the type just described which is illustrated in the accompanying drawing in Fig. 1 having a cellulose acetate base, it is exposed normally in a camera to a natural color scene as shown in Fig. 2 after which it is given a development treatment in a bath containing an ordinary or non-color-forming developing agent. Any suitable developer may be used at this stage such as the "first developer" of a color-reversal process, but preferably the developer is an energetic-working developer, such as is used with positive or X-ray films. It is also desirable that the developer selected produce a minimum of relief effect in the gelatin. To this end, caustic alkalies should be avoided. Sodium carbonate is a good alkali and is used in amounts smaller than generally used reversal "first developers." "Metol" in combination with hydroquinone, for instance, is suitable as the developing agent as are acid amidol developers. The development at this stage should be carried out completely, that is none of the latent images should be left undeveloped.

After development and washing, the film consists of three color separation negative image layers bearing both silver and unexposed and undeveloped silver salt images, and two layers of black metallic silver in which there may be small amounts of noncolor sensitized silver salts. The film at this stage which is shown in Fig. 3 of the drawing is now preferably exposed through the base with a red or white printing light which exposes only the silver-salt image remaining in the red sensitive layer. The characteristics of the film after this treatment are shown in Fig. 4. The printing light does not affect the other layers because the black metallic silver barrier layer prevents substantially all the printing light from passing through to other layers. A red printing light is advantageous because it does not affect the other two layers because of their lack of sensitivity to such light.

The film is now color developed in a minus-red or blue-green color forming developer, a suitable developer for this purpose being as follows:

Color-developer A

Potassium carbonate	grams	40
Sodium sulfite, anhy	do	5
Di-ethyl-paraphenylenediamine hydrochloride	grams	3
Water to	liter	1

to which is added a solution of

2:3:4-trichlor-alpha naphthol	grams	2
Ethyl alcohol	cubic centimeters	25

This developer forms both silver and minus-dye images from the exposed silver-halide of only the red-sensitive layer. The film which is illustrated in Fig. 5 is then thoroughly washed.

The top, or blue-sensitive layer, is now exposed to a blue or white (preferably white) printing light which treatment results in a film having the characteristics shown in Fig. 6. The printing light does not print-in the middle layer because of the metallic silver barrier layer between the top and middle layers. The entire film is then treated with a minus-blue color-forming developer, a suitable formula for such a developer being:

Color-developer B

Potassium carbonate	grams	40
Sodium sulfite, anhy	do	5
Diethyl-paraphenylenediamine hydrochloride	grams	3
Water to	liter	1

to which is added the following solution:

Benzoylacet-p-aminophenylmorpholine, dissolved in 25 cc. ethyl alcohol	grams	3

After development, the blue-sensitive layer will contain both metallic silver and yellow dye images. The film at this stage is illustrated in Fig. 7.

There now remains the green-sensitive middle layer on both sides of which are black metallic silver barrier layers. The central layer is preferably chemically exposed by bathing the film in a solution of a mild reducing agent, e. g. 0.5% aqueous solution of alkaline sodium arsenite, a 5% solution of hydrogen peroxide, etc. Such chemical exposures make the silver salts remaining in the middle layer developable and results in a film as shown in Fig. 8.

As another means of chemical exposure the film may be treated with an aqueous solution of an organic sulfur-bearing compound such as a 5% aqueous solution of guanidine thiocyanate or guanyl thiourea, thiourea, allyl thiourea, iminoamino methane sulfinic acid of a pH of approximately 6.8.

It is not necessary, however, to resort to chemical exposure of the middle layer to render it exposed or so that the silver salts are sensitized. Thus, the middle layer may be exposed by means of non-visible energy radiations, such as X-rays, heat rays or ultra-sonic vibrations passing through the entire film. In the latter case the entire film, during the latter part of the washing operation following the yellow development, may be subjected to ultrasonic vibrations, or the film, after washing may be immersed in water or some non-film solvent and then subjected to ultra-sonic vibrations. The central layer can also be exposed by means of heat rays, in which case the entire film should be immersed in 5% formaldehyde solution before exposing to the heat rays.

After the middle layer has been exposed, the entire film is treated or developed in a solution containing a developing agent, a magenta or minus-green color former to form a magenta dye upon development, a suitable solution for which is as follows:

Color-developer C

Potassium carbonate	grams	40
Sodium sulfite, anhy	do	5
Diethyl-paraphenylenediamine, hydrochloride	grams	3
Water to	liter	1

to which is added the following:

1-naphthyl-3-methyl-5-pyrazolone	grams	3
Ethyl alcohol	cubic centimeters	25

After this final development the film has the characteristics shown in Fig. 9. The silver is then removed from all the layers by means of such well-known reducers as Farmer's Reducer, used either as a combined bath or separately, by immersing the film in a 5% solution of potassium

ferricyanide and then immersing in a 20–40% sodium thiosulfate solution. The resulting film and the reproduction of a colored object therefrom is shown in Fig. 10.

In a modification of the invention which is of considerable importance, a green-blind, red-sensitive layer occupies the central position of the multilayer film. This green-blind, red-sensitive layer may be so sensitized by means of pinacyanol, one of the naphthoseleno carbocyanines described in Middleton and Dawson application, Serial No. 78,734, filed May 8, 1936, the unsymmetrical carbocyanines derived from lepidine derivatives and naphthothiazole quaternary salts described in Middleton and Jennings application, Serial No. 174,114, or the green blind sensitizing dyes of U. S. Patents Nos. 2,148,979, 2,148,980 and 2,071,898. The multilayer film used in this modification consists of a support coated on one side with a green sensitive emulsion, then a pre-fogged silver salt layer on which is coated a green-blind, red-sensitive emulsion layer on which is coated another fogged silver salt, on which is coated a blue-sensitive layer. The last-mentioned layer may contain a yellow filtering agent or it may be incorporated in a separate colloid layer, e. g. a gelatin sublayer, or in the layer of fogged silver salts.

In using the just-described film, it is exposed in a camera to a color scene with the emulsion facing the lens. It is then processed to color image records by the following steps:

1. Develop in a contrasty non-color-forming or ordinary developer, e. g. any of the well-known "first" developers of a reversal process.

2. After washing, the film is flashed through the case with white or green light which exposes the green sensitive layer but not the red or blue layers due to the barrier layer of metallic silver formed by the first development.

3. The film is developed in a magenta color-forming developer, such as "Color-developer C" of the preferred procedure.

4. After removing the developer from the film by washing the emulsion side of the film is flashed with white light which exposes the outside layer.

5. The film is now developed in a yellow color-forming developer such as, for example, "Color-developer B" in the preferred form, and followed by a 5 minute development in "Rodinol" diluted 1 to 3 aparts of water or an amidol developer to develop up any residual latent images.

6. After freeing the film of developer by washing, the film is subjected to X-ray exposure, a suitable exposure being 90 M. A. S. at 6 inches from an X-ray tube operating at 70 K. U. P.

7. The film is now developed in a blue-green color-forming developer, such as is given under "Color-developer A" in the preferred form.

8. After washing the silver deposits in the different layers are removed by means of a reducing agent such as Farmer's Reducer or by treatment with cupric bromide, followed by a clearing bath of hypo and the final wash.

A film similar to that just described which has the green sensitive layer on one side of the base and the green-blind red sensitive and blue sensitive layers on the other side of the base may be processed in a manner similar to the immediately preceding type of film. In this modification a pre-fogged layer is placed between the green sensitive layer and the base but no prefogged layers are placed upon the other side between the green-blind and blue sensitive layers. A yellow filter layer is coated over the red-sensitive layer; in processing, blue-light or ultraviolet exposure is given the outside layer.

Another film construction which can be processed by the processes hereof comprises a film base having a pre-fogged layer, preferably containing a red dye, on one side of a transparent film base over which is coated a red sensitive layer. On the other side of the base is first a green sensitive layer, next a prefogged silver halide layer and finally a blue sensitive layer which preferably contains a yellow filtering agent or has a layer containing such a layer in intimate contact therewith.

The invention hereof, however, is not limited to three color photography, but on the contrary may be used in two color photography wherein a pre-fogged layer is placed between two differentially sensitized layers either directly by reason of one layer being disposed on the opposite side of the base. Such films are processed in the same general manner described above, namely, development in a non-color-forming developer and subsequent flashing to light and color development of the layers on respective sides of the black silver barrier layers.

A film similar to that used in the preceding modification is employed for the preparation of multicolor positive prints. In this modification, three color-separation negatives are required. These may be made either in a camera or from a colored transparency or from a colored reflection print by reflection copying. Positive prints in black and white may be made from these negatives or the negatives themselves may be reversed into positive records. Three positive separation records are printed onto the multi-layer film previously described in the preceding modification. The sequence of printing operations is not important but the following serves as illustrative of a preferred procedure:

(*a*) The blue record positive is printed by white or blue light onto the top layer.

(*b*) Red record positive is printed by orange red light, through the top layer onto the central layer.

(*c*) The green record positive is printed by green or white light, through the base onto the bottom layer.

(*d*) The film is developed in an ordinary developer, such as the "first" developer of a reversal process and the film is processed to color by following through the steps two to eight inclusive as described in the preceding modification.

In place of the specific aromatic amino developing agents described in the preceding examples may be substituted various other specific agents of this type. These agents have an unsubstituted amino group which apparently enables the oxidation product to couple with the color-forming compound. Such agents include the di- and triamino aryl compounds in which one amino group is in the ortho or para position to another amino group, and the compounds formed therefrom by substitution in the amino group as well as in the ring. Thus, halogen, alkyl, alkoxy and aryl groups may be present.

The preferred developing agents in the process of dye coupling development are derivatives of p-phenylenediamine and particularly the asymmetric dialkyl p-phenylenediamines of 1 to 4 carbon atoms, e. g., p-aminodimethylaniline, p-aminodiethylaniline, p-aminodibutylaniline, etc. Other developing agents which may be used include p-phenylenediamine itself, p-methyl-

aminoaniline, p-ethylaminoaniline and p-aminophenol, N,N-diethyl-o-phenylenediamine, chloro-p-phenylenediamine, 1,2,5-toluylenediamine, 2-amino-5-diethylaminotoluene, N-p-aminophenyl-piperidine, N-methyl-N-hydroxyethyl-p-phenylenediamine, N-butyl-N-hydroxyethyl-p-phenylenediamine, 2-amino-5-(N-butyl-N-hydroxyethyl) aminotoluene and its dihydrochloride, β-γ-dihydroxypropyl-p-phenylenediamine, 4:4'-diamino-diphenylamine, 4:4'-diamino-2'-hydroxy-diphenylamine, etc. These aromatic amino-developing agents are in the form of their organic or inorganic acid salts and may be used in the preparation of the developing solutions. The salts are in general more stable than the free bases. As examples of suitable salts mention is made of the hydrochloride, sulfates, acetates, etc.

Likewise, other color forming compounds or mixtures may be substituted for the specific ones set forth in the above procedures and color developer baths.

As examples of representative suitable yellow color-formers which are soluble or readily dispersible in the reducing solutions are diacylacetamino-aryl-bis-thiazoles of U. S. Patent 2,140,540, of which difuroylacetamino-1,2,4,5-benzo-bis-thiazole is preferred, the acylacetarylides of U. S. Patent 2,108,602, acetyl acetone, β-naphthoyl acetone, aceto-acetic esters, ethyl α-chloroacetoacetate, ethyl γ-chloro-acetoacetate, ethyl malonate, ethyl-p-nitrophenyl-acetate, ethyl acetopropionate, ethyl acetone dicarboxylate, furoylacetic ester, the acyletamino phenyl morpholines of U. S. Patent 2,133,937, etc.

Suitable magenta color-formers include nitriles, e. g. p-nitrobenzyl cyanide, o-nitro-benzyl-cyanide, p-toluyl-acetonitrile, ω-cyanoacetyl-dibenzfuran, ω-cyano-acetylacenaphthene, 1-ω-cyano-acetylcoumarone, 1:3-di-(ω-cyanoacetyl)-benzene, acyl nitriles, e. g. cyanacetophenone, methoxy-α-naphthoylacetonitrile, cyanacetanilides, e. g. 1-cyanacetaminobenzthiazole, etc., phenyl- and naphthyl-methyl-pyrazolones, e. g. 1-phenyl- and 1-naphthyl-3-methyl-4-pyrazolone.

Suitable blue-green color formers include phenols, e. g. ortho and meta-chlorophenol, o-bromophenol, o-iodophenol; naphthols, e. g. 2,3,4-trichlornaphthols, 2,6-dibromo-1,5-dihydroxy naphthalene, etc. Other color-formers will be apparent to those skilled in the art.

The present invention has a number of distinct advantages over prior art procedures. Thus it enables one to control the extent to which each color-contributing layer of the monopack is developable by controlling the amount of second or flashing exposure given each layer.

By the present invention the blue-green contributing layer is not prematurely fogged with the attendant disadvantages. This constitutes an improvement over processes and films of the prior art wherein a "buried" layer is optically isolated by dye-filter layers alone. In such instances, the blue-green contributing layer is almost invariably prematurely fogged due to the fact that no water soluble or developer dischargeable red dyes are known which do not pass some blue light.

A further advantage resides in the fact that processing steps which require a complicated controlled diffusion of processing baths are eliminated.

The resulting processed film is free of any residual or non-used color-forming material.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that it is not intended to be limited to the specific embodiments herein, except as defined by the appended claims.

We claim:

1. A method of color photography which comprises developing a photographic element comprising a transparent base having at least two differentially sensitized silver halide emulsion layers superimposed thereon, one of the layers being imposed directly on the base and a layer of pre-fogged silver salts interposed between said emulsion layers, with a non-color-forming developer whereby silver images are formed in the emulsion layers and on opaque barrier layer is simultaneously formed, exposing an outer silver halide layer to light and color developing the same, treating the central silver halide layer to render the silver salts developable and color developing it and removing the developed silver from all layers.

2. A method of color photography which comprises developing a photographic element comprising a transparent base having three differentially sensitized silver halide emulsion layers superimposed thereon, one of said layers being imposed directly on the base and a fogged silver salt layer between each of said emulsion layers; with a non-color-forming developer, whereby silver images are formed in the emulsion layers and opaque barrier layers are simultaneously formed, respectively exposing and color developing the outer silver halide layers, treating the central silver halide layer to render the silver salts developable and color developing said central layer.

3. A process as set forth in claim 1 wherein the silver halide layers are respectively first exposed to light and then color developed to form reverse dye images.

4. A process as set forth in claim 2 wherein the two outer layers are respectively exposed to light and color developed and the middle layer is chemically exposed and color developed.

5. A process as set forth in claim 2 wherein the two outer layers are respectively exposed to light and color developed and the middle layer is exposed by non-visible radiant energy and color developed.

6. A method of color photography which comprises developing a photographic element comprising a transparent base having three silver halide emulsions sensitized red, green and blue, respectively, superposed thereon, the red layer being imposed directly on the base, a pre-fogged silver salt layer interposed between each of the emulsion layers and a yellow filtering layer positioned in front of said red sensitized layer, with a non-color-forming developer whereby silver images are formed in said emulsion layers and opaque barrier layers are formed, re-exposing to light containing red light the silver salts in the red layer and color developing the reversed image blue-green, re-exposing the blue sensitive layer to light containing blue light and color developing the image yellow, chemically re-exposing the middle layer and color developing it magenta and removing the silver from each of the layers.

7. A method of color photogrphy which comprises developing a monopack comprising a transparent base, a green sensitized silver halide emulsion layer imposed directly on said base, a pre-fogged silver salt layer imposed on said green, a green-blind panchromatic emulsion layer im-

posed on said pre-fogged layer and a blue sensitized emulsion layer imposed upon said panchromatic layer; with a non-color-forming developer agent, re-exposing the element through the base with light containing green light and color developing said layer. Magenta, re-exposing the central layer to orange red light and color developing it blue-green, re-exposing said element to light containing blue light and color-developing said layer yellow, and removing the silver deposits from all layers.

8. A process as set forth in claim 7 wherein the blue sensitized layer contains a yellow filter dye.

9. A process as set forth in claim 2 wherein the respective layers are color developed to images which are complementary in color to the utilized respective sensitivity of the emulsion layers.

10. A process as set forth in claim 2 wherein the silver salts in said central layer are made developable by treatment with a fogging agent after color development of at least one of the remaining component images.

11. A process as set forth in claim 2 wherein the silver salts in said central layer are made developable by treatment with a fogging agent after color developing each of the outer silver halide layers.

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CERTIFICATE OF CORRECTION.

Patent No. 2,262,055. November 11, 1941.

VIRGIL B. SEASE ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 4, second column, line 70, claim 7, for "photogrphy" read --photography--; page 5, first column, line 6, claim 7, for "layer. Magenta" read --layer magenta--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 30th day of December, A. D. 1941.

Henry Van Arsdale,
Acting Commissioner of Patents.

(Seal)