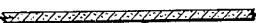


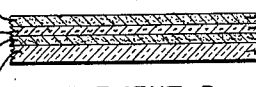
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PHOTOGRAPHIC FOUR-COLOR LIGHT-SENSITIVE
STRIPPING ELEMENTS
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2,492,952

5  YELLOW FILTER ELEMENT

4  3 SILVER HALIDE LAYER GREEN-SENSITIVE-MAXIMUM 490-535 mμ.
2 STRIPPING LAYER
1 SILVER HALIDE LAYER RED-SENSITIVE-MAXIMUM 605-670 mμ.
FILM BASE
ELEMENT-A

8  7 SILVER HALIDE LAYER SENSITIVE BLUE & VIOLET LIGHT
6 STRIPPING LAYER + DYE ABSORBING LIGHT BELOW 540 mμ.
5 SILVER HALIDE - SENSITIVE TO YELLOW MAXIMUM 545-575 mμ.
4 FILM BASE
ELEMENT-B

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PHOTOGRAPHIC FOUR-COLOR LIGHT-SENSITIVE STRIPPING ELEMENTS

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3 Claims. (Cl. 95—2)

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This invention is concerned with color photography. More particularly, it is concerned with photographic elements for processes of photography and to processes of producing images therein.

An object of this invention is to provide new and useful photographic elements. A further object is to provide photographic films for the recording of multicolor scenes. A still further object is to provide practical elements for processes of four-color photography. A related object is to provide such elements which can be readily processed to form four separate color separation negatives. Still other objects will be apparent from the following description of the invention.

The composite pair of photographic elements of this invention consist of two separate film elements which are adapted for simultaneous use in a beam-splitting camera to record a multicolor picture. Each film element bears two differentially sensitized colloid silver halide emulsion layers at least one of which is strippable from the remaining support. The layers are sensitized respectively to different narrow regions of wave lengths of light in the visible spectrum and are so arranged that the two films when used in a beam-splitting camera record light from four separate and distinct regions of the visible spectrum.

The novel photographic film elements of this invention will be further described with reference to the accompanying drawing which constitutes a part of the present specification. Referring now to the drawing, film elements of the invention consist of element A consisting of a transparent film base 1 which may be composed of a cellulose derivative, e. g., cellulose nitrate, cellulose acetate, cellulose acetate propionate, cellulose propionate; a synthetic resin, e. g., polyvinyl chloride, polyvinyl chloride acetate, polymerized methylmethacrylate; or a superpolymer, e. g., nylon, is provided with a light-sensitive layer 2 composed of a water-permeable colloid having intimately dispersed therethrough light-sensitive silver halides which are sensitive to light in the red region of the spectrum and have a maximum sensitivity in the range 605 to 670 millimicrons. A stripping layer 3 is disposed on the light-sensitive layer 2 and serves as an intermediate support for a water-permeable colloid silver halide emulsion layer 4 which is sensitized to green light and has a maximum sensitivity in the range 490 to 535 millimicrons. A yellow filter

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element 5 which absorbs light in the blue region of the spectrum is placed before element A when it is ready for exposure in the camera. This filter may be in the form of a layer which is coated on light-sensitive layer 4 or may be a separate layer. In either case, it may consist of a colloid, e. g., gelatin, which contains a yellow filter dye or pigment.

Film element B consists of a transparent film base 1' similar to base 1 of element A which bears a light-sensitive silver halide emulsion layer 6 which is sensitive to yellow light and possesses its maximum sensitivity in the range 545 to 575 millimicrons. A stripping layer 7 is coated onto the emulsion layer. This stripping layer contains a yellow-orange filter dye or pigment which is capable of absorbing or screening light shorter than 540 millimicrons while passing all other wave lengths. A silver halide emulsion layer 8 which is sensitive to blue and violet light only is disposed on the stripping layer.

In operation, the two film elements are disposed in the optical system of a beam-splitting camera. One of the films is placed at one recording aperture and the other at the other recording aperture of the camera. The light coming from the multicolor scene or object is split into two parts and the split beam which contains the blue and yellow wave lengths of light are recorded in film element B whereas the split beam which contains the green and red wave lengths of light are recorded in film element A at the respective camera aperture.

The beam-splitting cameras, of course, do not constitute a part of the present invention. They may be of varied type and construction. Suitable types are disclosed in United States Patents 1,889,030, 2,000,058, 2,072,091 and 2,270,749.

It is to be understood that each of the silver halide emulsion layers are inherently sensitive to blue light, in addition to having the extra sensitivity specified above. However, the light filter layers prevent the lower layers from being exposed in the blue region of the spectrum.

The novel photographic elements of this invention are especially useful in the processes of four-color photography disclosed in Ball application Serial Number 771,790, filed September 2, 1947. The photographic elements can be used to form four individual color separation records from which four color separation positive silver image records can be printed as provided in said application. The latter image records can then

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be converted into colored images having the absorption peaks and characteristics taught in said application. The colored images may then be superimposed in register to reproduce a multi-color picture.

The stripping layers of the elements may be composed of various materials which are softened or dissolved by water. Thus, they may be composed of any water-soluble colloid (viz. which has a marked solubility in water at 20° C.) of natural or synthetic type. Suitable colloids include water-soluble cellulose derivatives, e. g., low substituted cellulose ethers, such as methyl cellulose, ethyl cellulose, and benzyl cellulose; cellulose esters having solubilizing acid salt groups, e. g., sodium, potassium, and ammonium salts of cellulose acid phthalate; cellulose ether acids, e. g., sodium cellulose glycollate, casein gelatin mixtures; water-soluble synthetic resins, e. g., polyvinyl alcohol and esters.

In the preferred aspect of the invention, the stripping layers are composed of a water-soluble but photographic alkaline developer insoluble colloid. Preferred colloids of this type are composed of water-soluble macromolecular acetals of vinyl alcohol polymers with an aldehyde containing sulfonic acid and/or carboxylic acid groups or their water-soluble salts, e. g., alkali metal, ammonium, or amine salts.

The water-soluble macromolecular acetals can be made by the reaction of a vinyl alcohol polymer, including interpolymers, with an aldehyde containing a sulfonic acid or a carboxylic acid group under acetal forming conditions. For example, the acetalization may be conveniently carried out in solution or suspension in water or an organic solvent or diluent using a catalyst such as phosphoric acid, sulfuric acid, hydrochloric acid, etc. Suitable procedures and aldehydes are described in United States Patent 2,310,943 and in German Patent No. 643,650. The free acid groups can be converted into salt groups by a simple neutralization as described above and in the United States patent. Preferred acetals are disclosed in application Serial Number 658,224 filed March 29, 1946, now Patent No. 2,462,534 of Feb. 22, 1949.

The colloid stripping materials e. g., the water-soluble macromolecular acetals of vinyl alcohol polymers described above can be applied to the contiguous layer from a solution or dispersion in the same general manner that gelatin overcoatings are applied. The acetal layers so applied should be of such a thickness that the emulsion layers joined thereby may be readily stripped from one another. The exact thicknesses can be readily determined by experiment. Thicknesses of 2.5 to 12.5 microns, in general, are satisfactory. Materially thinner layers, e. g., 0.05 to 2.0 microns, in general, adhere quite firmly. They may be applied from aqueous or organic solvent solutions. Useful solvents are methanol, ethanol, acetone, dioxane, etc. Mixtures of such solvents with water are quite useful. The coating solutions are preferably substantially neutral. Their pH can be adjusted by neutralizing the free acid groups with bases capable of yielding water-soluble salts, e. g., alkali metal hydroxides, ammonia, and amines. Various filter dyes or pigments may be added to the coating solutions prior to depositing the layers on the silver halide emulsion layers.

The film elements, after exposure in the beam-splitting camera, are then developed to produce images in the various light-sensitive layers. The

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two films need not be fixed before further processing as this may be conveniently done later. The outer layers of the respective developed front and rear film elements are pressed into intimate

contact with a second registered support, e. g., a transparent film base coated with a gelatin layer which may be wetted with water to promote adhesion with the outer layer of said front or rear films of the bipack. Wetting the gelatin layer is not essential and in some cases may be omitted to advantage. The water weakens the bond between the said outer layer and the stripping layer whereby the outer layer is stripped off and transferred to the support. An alternative procedure may be used in which the stripping operation precedes development. This leaves four separate color separation records which can be converted into colored images in any desired manner or they may be fixed, washed, and dried and used to print positive image color separation records which can be converted into colored image records by color coupling development utilizing color formers which yield quinoneimine or azomethine dyes, followed by fixing, washing, and drying. The various four-color methods of reproducing multicolor images disclosed in the aforesaid Ball application can be resorted to. The four dye or colored image positive records are then superposed in register which results in a multicolor positive picture.

The following example will serve to further illustrate the invention.

Example.

A cellulose acetate film which has a thin gelatin-nitrocellulose anchoring substratum is coated with a red-sensitive gelatino-silver bromide emulsion which contains 5, 5', 9-trimethyl thiocarbocyanine iodide and possesses its maximum sensitivity at 640 to 650 millimicrons to a coating weight of 50 milligrams of AgBr per square decimeter. An aqueous alcohol solution of a water-soluble, developer insoluble o-sulfobenzaldehyde acetal of polyvinyl alcohol is coated onto the emulsion layer to a thickness of about five microns. A green-sensitive gelatino-silver bromide emulsion which is sensitized with 3, 3'-diethyl-9-methyl exycarbocyanine iodide and has its maximum sensitivity at 514 to 520 millimicrons is coated onto the stripping layer to a coating weight of 50 milligrams of silver bromide per square decimeter. The resulting element constitutes film A of the composite pair.

Another cellulose acetate film which is provided with a thin gelatin-nitrocellulose anchoring substratum is coated with a green-sensitive gelatino-silver bromide emulsion which contains 3, 3'-diethyl naphthoxycarbocyanine iodide and possesses its maximum sensitivity at 570 millimicrons to form a layer having a coating weight of about 50 milligrams per square decimeter. An aqueous alcohol solution of a water-soluble, developer-insoluble o-sulfobenzaldehyde acetal of polyvinyl alcohol which has dispersed therethrough 0.05 part of Wool Orange A (Colour Index #151) per part of acetal is coated onto the emulsion layer to form a stripping layer about three to ten microns thick. A blue-sensitive gelatino-silver halide emulsion layer is coated onto the stripping layer. The film element so prepared constitutes element B as described above.

The "Color Index" herein referred to is that by F. M. Rowe, publ. by The Society of Dyers and Colorists, England, first ed., Jan. 1924.

The resulting composite pair of elements is exposed in a beam-splitting camera as described above by placing a yellow filter before film A at the respective beam-splitting aperture and exposed to a multicolor object field thereby forming color component latent image records in the respective light-sensitive records. The elements are then developed for seven minutes in a solution made by admixing the following components:

Hydroquinone	grams	7.5
p-N-methylaminophenol sulfate	do	5.0
Sodium sulfite (anhydrous)	do	60.0
Sodium carbonate (anhydrous)	do	50.0
Potassium bromide	do	15.0
Water to	liter	1.0
The developed films are then treated for three minutes in a stop bath of the composition:		
Volumes		
Acetic acid (28%)		1.0
Water		20.0

In some cases it has been found desirable to add inert salts such as sodium sulfate (about 120 grams per liter) to the stop bath to prevent excessive softening of the stripping layer. The outer layer of the respective films is then pressed into intimate contact with a second registered support comprising a transparent film base coated with a gelatin layer having a coating weight of about 75 milligrams per square decimeter which had been wetted with water to promote adhesion between the surfaces. In some instances the use of a dry gelatin blank promotes more rapid adhesion. The water weakens the bond between the outer layer and the stripping layer so that it may be stripped and transferred to said gelatin coated support.

In place of the sensitizing dye for the inner emulsion layer of film A, there may be substituted various other sensitizing dyes which will confer similar sensitizing properties. Among such dyes are 3, 3'-diethylselenocarbocyanine iodide and 2-(p-dimethylaminostyryl)-6-ethoxy benzothiazole ethyl bromide.

Similarly in place of the specific sensitizing dyes for the outer layer of element A, there may be substituted other dyes, e. g., 3, 3'-diethyl oxycarbocyanine iodide and 3, 3'-diethyl-5, 5'-dimethylloxycarbocyanine iodide which confer similar sensitivity.

In like manner in place of the specific dye for the inner layer of element B, there may be used equivalent sensitizers including erythrosine, 3-ethyl-5-(3-ethyl-2 (3)-benzoxazolyldene) ethyldene rhodanine and 1, 1'-diethyl pseudocyanine-p-toluene sulfonate.

Various other dyes or pigments may be substituted for that in the stripping filter layer of element B in the above example. Another suitable dye includes Pontacyl Brilliant Orange 2R (Colour Index #216).

Various other stripping layers can be used in place of the specific acetal of the example. They may be composed of any of the materials described above for this purpose. Additional suitable coating compositions for this purpose include the following:

Solution A:		
Casein	grams	20.0
Water	cc	100.0
Na ₂ CO ₃ (20%)	cc	6.8
Gelatin	gram	1.0
Mannitan monolaurate (10%)	cc	5.0
Water	cc	50.0

Solution B:		
Corn dextrine	grams	10.0
Water	cc	100.0
Ethanol	cc	20.0
Saponin solution	cc	10.0
Aerosol CEL (10%)	cc	2.0

Solution C:		
Cellulose acetate-acid phthalate	grams	5.0
Na ₂ CO ₃	cc	10.0
Ethanol	cc	50.0
Water	cc	150.0
Gelatin	grams	5.0
Water	cc	100.0

It is to be understood, however, that the light-screening or filter dyes or pigments are to be added to said solutions before coating.

The silver halide emulsion layers are preferably composed of gelatin as the binding agent. However, various other natural or synthetic hydrophilic colloids can be used, if desired, e. g., agar agar, albumin, nylon, polyvinyl acetals, the hydrolyzed ethylene/vinyl acetate interpolymers of United States Patent 2,397,866, etc.

The film elements of this invention are new and useful in processes of four-color photography. They are simple in construction yet effective in operation. They can be made by using the conventional coating apparatus and procedures and utilize economical materials in the stripping layers.

The use of a split-beam camera and two monopack films as described, in contrast to the conventional bipack exposure system and film elements, possesses several advantages. The method permits exposures to be made on the emulsion side of the film of both elements instead of exposing through the base as in the conventional bipack system. The resulting images are sharper even in the rear layers and less exposure is required.

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

What is claimed is:

1. A composite pair of film elements comprising a film base having superposed thereon in order a water-permeable colloid silver halide emulsion layer which has an extra band of sensitivity in the red region of the spectrum with a maximum at a position within the range from 605 to 670 millimicrons, a stripping separator layer composed of a developer-insoluble, water-soluble colloid and a water-permeable colloid silver halide emulsion layer having a band of extra sensitivity in the green region of the spectrum with a maximum at a position between 490 and 535 millimicrons, and a film base having superposed thereon in order a water-permeable colloid silver halide emulsion layer having a band of extra sensitivity in the yellow region of the spectrum with a maximum at a position within the range from 545 to 575 millimicrons, a stripping separator layer composed of developer-insoluble, water-soluble colloid containing a yellow-orange filtering material which absorbs light shorter than 540 millimicrons and passes longer wavelengths and an outer water-permeable colloid silver halide emulsion layer sensitive to blue light only.

2. A composite pair of film elements as set forth in claim 1 wherein the colloid of said emulsion layers is gelatin.

3. An element as set forth in claim 1 wherein said silver halide emulsion layers contain gelatin as the binding agent and the stripping layers are composed of a water-soluble acetal of a vinyl alcohol polymer with an aldehyde containing a group taken from the class consisting of free carboxylic acid groups, free sulfonic acid groups, and their water-soluble salts.

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