June 6, 1944. C. F. A. WHITE 2,350,380

PHOTOGRAPHY

Filed Aug. 1, 1940 2 Sheets-Sheet 1

Fig. 1

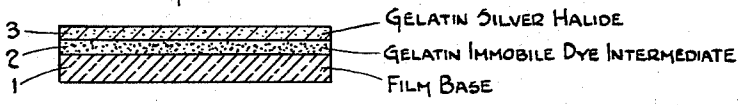


Fig. 2

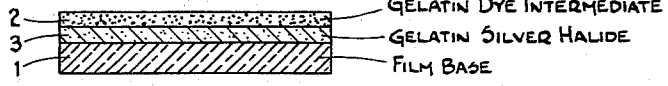


Fig. 3

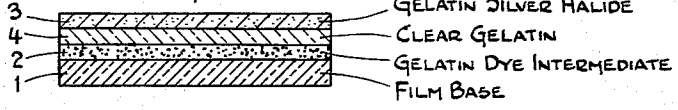


Fig. 4

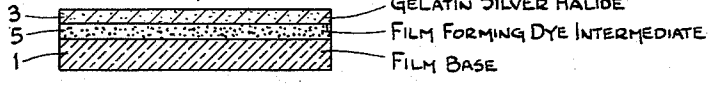


Fig. 5

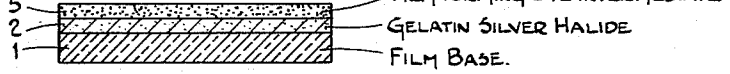


Fig. 6

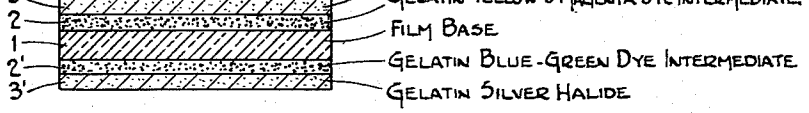
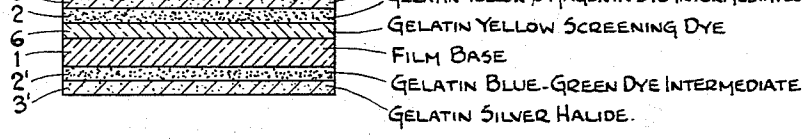


Fig. 7



Inventor

Clayton F.A.White

By Lyman B. Morris

Attorney

June 6, 1944. C. F. A. WHITE 2,350,380

PHOTOGRAPHY

Filed Aug. 1, 1940 2 Sheets-Sheet 2

Fig. 8

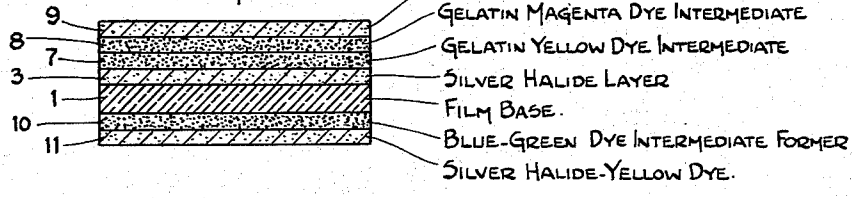


Fig. 9

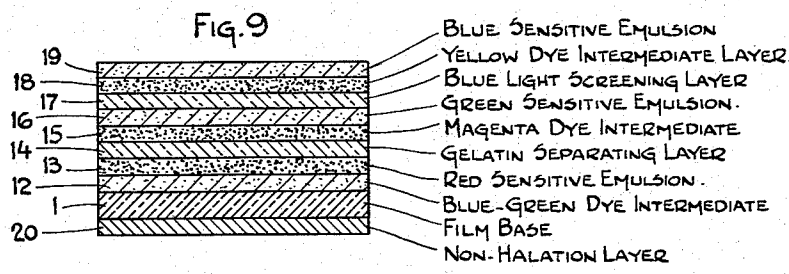


Fig. 10

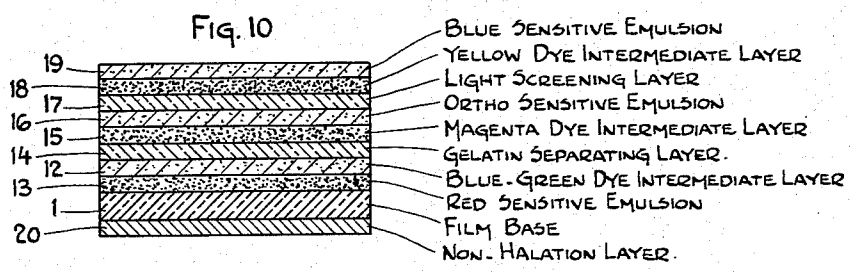
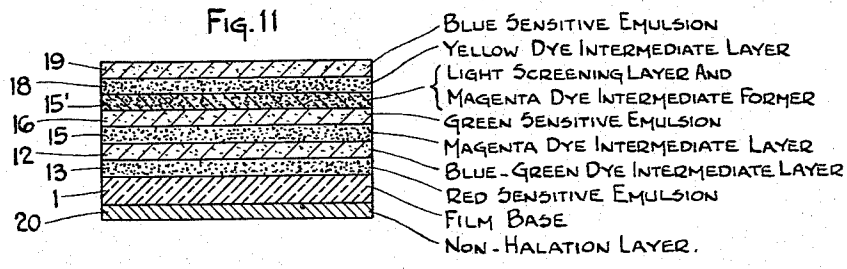


Fig. 11



Inventor

Clayton F. A. White

By Lynn B. Morris

Attorney

Patented June 6, 1944 2,350,380

UNITED STATES PATENT OFFICE

2,350,380

PHOTOGRAPHY

Clayton F. A. White, Stelton, N. J., assignor, by mesne assignments, to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

Application August 1, 1940, Serial No. 349,228

6 Claims. (Cl. 95—2)

This invention relates to color photography, and more particularly to multicolor photography. It further relates to new and improved photographic elements for use in the production of color images. More particularly it relates to photographic films and plates for the production of multicolor photographs. Still more particularly it relates to photographic elements containing light sensitive layers and layers comprising dyestuff components which are capable of forming an indophenol, indoaniline or azomethine dye and also an azo dye. The invention also relates to processes for the production of color images in such elements.

At the present time there are a great many types of processes of color photography wherein colored images are formed. They are quite diverse in character. Some require a large number of processing steps which is uneconomical, require excessive processing treatment, and do not result in sharp, true color images.

Many promising processes for producing colored images involve the use of color formers or dye intermediates which form azomethine or quinoneimine dyestuffs upon development of exposed or latent silver images with primary aromatic amino developing agents. The color-formers are incorporated in light sensitive emulsion layers which in the case of 3-color photography, are so arranged and sensitized that each layer will record about one third of the visible spectrum. In other related processes the light sensitive emulsions are mixed and the color formers are absorbed on the silver halide grains.

The just described elements and processes have a number of disadvantages in that many color formers (1) reduce the overall sensitivity of emulsions, (2) reduce or destroy the color sensitized characteristics of emulsions, (3) produce general emulsion fog. This is particularly true of the insoluble high molecular weight immobile or non-migratory type which are incorporated in emulsion layers. Others wander in emulsion layers and cause dilution of color.

This invention has for an object the production of new and useful photographic elements. A further object is to provide elements which will faithfully record a color scene. A still further object is to provide film elements in which a color scene can be faithfully reproduced. A still further object is to provide film elements which can be successfully processed to colored images by a minimum number of processing steps. Another object is to provide a multilayer film which can be processed without excess handling thereof.

A further object is to provide novel methods of developing or forming colored images in multilayer films. A further object is to provide a reversal process for producing color images in an exposed multilayer element involving a few simple steps. Another object is to provide a process for simultaneously producing colored images in unsensitized layers in a photographic element. Still other objects will appear hereinafter.

The above objects are accomplished and the mentioned disadvantages overcome by the hereinafter described invention which in its broader aspects comprises the production and use of photographic elements comprising reducible silver salt, generally a silver halide, coating or layer and at least one co-acting strata or layer which may be in contact therewith or spaced therefrom, comprising an immobile dye intermediate or color former capable of forming a quinoneimine dye e. g. an indophenol, indoaniline or an azomethine dye upon color forming development and an azo dye as the reverse image upon appropriate treatment.

Suitable elements comprise a base and at least two co-acting layers, one of which comprises a reducible silver salt and the other of which comprises an immobile dye intermediate or color former. The immobile dye intermediate or color former layer may be of two general types: (1) composed of an immobile dye intermediate or color former uniformly distributed or dispersed in a water permeable binding or supporting agent, and (2) composed of a film forming material containing within its structure dye forming nuclei, i. e. nuclei capable of forming an indophenol, indoaniline or azomethine dye and also an azo dye upon appropriate treatment. In this embodiment the dye intermediate color former itself constitutes a layer or strata of the film.

It will be obvious from the general considerations above that the invention is of considerable scope and not limited to one or two specific types of photographic elements or processes. On the contrary, it embodies many aspects and many modifications can be made. In all such elements, however, the immobile dye intermediate or color former layers or strata are separate from their co-acting reducible silver salt layers but do not have any water impermeable layers or membranes therebetween. The dye intermediate or color former layer or layers and co-

acting silver salt layer constitutes a color yielding unit. A plurality of color units are used in the elements herein described which are useful for multicolor photography.

In one embodiment of the invention the dye intermediate or color former layers are immediately adjacent the silver salt layers. One or more color former or dye intermediate layers may co-act with a single silver salt layer and constitute a single color yielding unit. Thus, color former layers may be placed on each side of the silver salt layer. The color formers may yield dyes of identical color or different colors which form a composite dye image of the proper color. For instance, one predominately blue and the other predominately green may be used for the blue-green unit.

In another embodiment of the invention the color-former layers are separated from respective co-acting reducible silver salt layers by a light transparent strata or layer composed of a substantially water insoluble, water permeable material or colloid. Suitable materials are cellulose derivatives, e. g. lower alkylethers, esters, glycollates, etc., regenerated cellulose, gelatin, agar-agar, etc.

The more complex ramifications of the invention will be more readily understood by the following description of the preparation and color processing of a simple two layer film element. A cellulose acetate film base is coated with a gelatino-silver bromide emulsion to form a thin coating or layer. A thin coating of the resinous color former such as salicylaldehyde acetal of polyvinyl alcohol is superimposed over the emulsion layer. The film element is exposed to record an object image, then developed with a color forming developing agent, for example, in a developer solution containing a primary aromatic amino developing agent, whereupon a silver image is formed in the original silver halide strata or layer and a colored image of an indophenol dye is formed in the contiguous color former or dye intermediate layer. Upon removal of the silver image the dye image remains solely in the contiguous layer.

A similar element may be processed to form a reverse dye image by first developing the exposed film in an ordinary or non-color forming developer. Then, the reverse image is developed with color-forming developing agent. Re-exposure, either chemical or physical, may be resorted to if desired prior to the "second" development. However, it is often advantageous to use an energetic dye forming reducing bath containing an organic nitrogeneous base having an association exponent of at least 9.0 and a primary amino developing agent. Suitable baths of this type are disclosed in Meschter application, Serial No. 295,685.

For multicolor photography, the elements may comprise a plurality of color yielding component units embodied in a single element which are so arranged and/or sensitive that each unit will produce a dye having a color corresponding to a different portion of the color spectrum. Each color component unit comprises a reducible silver salt layer or strata and at least one co-acting strata or layer in contact therewith containing at least one immobile dye intermediate capable of forming an indophenol, indoaniline or azomethine dye and also an azo dye therein.

In some modifications, each or one or more of the color component units may comprise two or more color yielding layers or strata which are preferably disposed on opposite sides of the reducible silver salt layer. The immobile dye intermediates or color formers in the layers are chosen so that together they form or each forms a composite dye image which is related in its color to the utilized sensitivity of the reducible silver salt layer in said unit. For color forming development processes the color formers or former form an indophenol, indoaniline or azomethine dye or composite dye image which is related in color to the utilized sensitivity of the respective unit. For azo reversal processes the color former or color formers are chosen so that they form an azo dye image or composite dye image which is related in color to the utilized sensitivity of the respective unit.

In the case of elements which are to be used in reversal processes of photography, the color former or color formers are chosen so that they form a dye image or composite dye image which is complementary in color to the utilized sensitivity of its respective unit. The color formers for use in color development reversal processes should be chosen so that they form indophenol, indoaniline or azomethine dyes complementary in color to the utilized sensitivity of the respective units. Similarly, for azo reversal processes, the color formers or dye intermediates should be chosen so that they form an azo dye or composite azo dye image which is complementary in color to the utilized sensitivity of the respective units.

Film elements useful as print stocks for color processes which do not have to meet all the requirements for the reproduction of a natural color scene by reversal methods, the color formers need not yield colors complementary to the utilized sensitivity of respective units. The arrangement of the units, type of scene or image to be reproduced, etc. have a definite bearing upon the choice of dyestuff component.

When two or more color yielding component units are used, it is often desirable that they be separated by an non-reactive layer, generally the film base. A practical two-color element, for instance, has the transparent base separating the sensitive layers and the co-acting color former layers are contiguous thereto. That is, at least one color yielding component unit is placed on each side of the base. Various modifications in structure may be made, but it is preferred that the light sensitive layers be innermost. In another practical element the two color yielding units are placed on the same side of the base. The base may be tinted and/or contain an antihalation strata or layer.

A practical 3-color element has two light sensitive layers with the contiguous co-acting color former layers or two color yielding component units separated by the transparent base. A third light sensitive layer is separated from the nearest emulsion layer by at least two layers. These may, of course, be the two respective color former layers. In a modified construction, a least one additional water permeable layer or strata separates the last-described two emulsion layers. In another practical 3-color element three color yielding units are placed on one side of the base. The base may be tinted and/or contain an antihalation strata or layer.

The color yielding units may contain various other photographic materials or strata. Thus, they may contain light filtering materials such as dyes or pigments or colloidal metals, e. g. colloidal silver, that is, silver in such a state that the single particles cannot be discerned with the aid of a microscope; which absorb certain wave lengths of

light. These materials may constitute separate layers or strata or they may be incorporated in the color former or dye intermediate layers or strata or in the light sensitive or silver salt layers or strata.

In many types of film elements for use in multicolor photography, it is desirable that a yellow screening dye be placed before the red and green recording layers so that they will not be exposed to the blue region of the spectrum, e. g. blue, violet and ultra violet. Suitable yellow screening materials include Tartrazine, Luxol Yellow, Naphthol Yellow, Auramine, cadmium sulfide, etc.

In film elements for multicolor photography it often is desirable to use red colored filtering materials (i. e. blue-green light absorbing) which are placed before the red recording layers. This obviates the necessity for green-blind sensitizing dyes. Suitable materials of this type include Congo red (C. I. 370), Carmosin M, uranine (C. I. 766), eosine (C. I. 768), xylene red B (Schultz No. 579), rose bengale (C. I. 777–779), etc.

The coating weights or thicknesses of the various layers, that is of the dye intermediate or color former layers, light sensitive or reducible silver salt layers and intermediate layers may vary over a wide range. The thickness used, of course, depends on many factors including the nature of the particular color former chosen, the water permeable binding or supporting agent or medium, the type of light sensitive silver salt and binding medium therefor, and the purpose for which the element is to be used.

A practical range of thicknesses for the dye intermediate or color former layer and/or composite wherein a water permeable binder or supporting agent is used may vary from about 1.5μ to about 5.0μ. A preferred range is about 2.0 to 4.0μ. In general a thicker layer is required for a print stock than for a reversal stock. A practical range of thicknesses for the emulsion or reducible silver salt layers may vary from about 2.0 to 6.0μ and a more preferred range from 2.0 to 4.0μ. The intervening layers may vary over an even wider range, however, a practical range may vary from 1.5 to 4.0μ.

The nature of representative elements and processes of the invention will be more readily understood by a consideration of the accompanying drawings in which,

Fig. 1 is a diagrammatical cross section of a film element for single color photographs and color component records.

Fig. 2 is a diagrammatic cross-section of a modified film element for single color photographs and color component records.

Fig. 3 is a diagrammatic cross-section of a modified film element for single color photographs and color component records having an isolating layer.

Fig. 4 is a diagrammatic cross-section of a film element for single color photographs having a film forming dye intermediate layer.

Fig. 5 is a diagrammatic cross-section of a modified film element having a film forming dye intermediate layer.

Fig. 6 is a diagrammatic cross-section of a film element for 2-color photography.

Fig. 7 is a diagrammatic cross-section of a modified film element for 2-color photography.

Fig. 8 is a diagrammatic cross-section of a further modified film element for 2-color photography, bearing a non-halation layer.

Fig. 9 is a diagrammatic cross-section of a film element for 3-color photography.

Fig. 10 is a diagrammatic cross-section of a modified film for 3-color photography.

Fig. 11 is a diagrammatic cross-section of a modified film for 3-color photography.

The invention shall now be further illustrated, but is not intended to be limited by the following examples:

Example 1

A film element (Fig. 1) comprising a cellulose nitrate base 1 is coated with a gelatin dispersion of salicylaldehyde-o-benzaldehydesulfonic acid-mixed acetal of polyvinyl alcohol to form a layer (2) from 3.5 to 5μ thick. The dispersion contains about 4.5 parts of gelatin per 2 parts of color former. A negative emulsion comprising silver bromide-iodide sensitized with 3,1'-diethyl-6'-ethoxy-α-naphthiocarbocyanine lepidine iodide is next coated upon layer (2) to form a light sensitive layer (3) about 2.5μ thick. The film is exposed to an object, then developed in a solution of the following composition:

p-Amino-N-diethylaniline hydrochloride	grams	4
Sodium sulfite (anhydrous)	do	3
Sodium carbonate	do	25
Water to	liter	1

The silver and residual silver salt are then removed by means of Farmer's reducer. A blue-green dye image of good strength and color is formed. A cross-section upon inspection under a microscope reveals that no color is present in the light sensitive layer.

Example 2

A film element as shown in Fig. 1 was prepared by coating the film base with a gelatin dispersion of 1 part of salicylaldehyde phthalaldehydic acid acetal of polyvinyl alcohol dispersed in about 5.3 parts of gelatin to a thickness of about 5.0. Next was coated an unsensitized silver bromide-iodide emulsion layer about 2.0μ thick.

The film element was exposed and developed in a solution prepared by mixing equal parts of the following solutions and further processed as in Example 1:

A.	Sodium sulfite	grams	2
	p-Amino-N-diethylaniline	do	4
	Metol	do	0.6
	Water to	liter	1
B.	Sodium carbonate	grams	40
	Water to	liter	1

Example 3

A film element identical with that set forth in Example 2 except that a gelatin dispersion containing 1 part of 1-(m-stearoylaminophenyl-phenyl)-3-methyl-5-pyrazolone per 4 parts of gelatin was used.

The element is exposed to an object and then treated as follows:

(*a*) Developed in a metol-hydroquinone developer of the following formula:

Metol	grams	1.4
Sodium sulfite, anhy	do	60.0
Hydroquinone	do	5.0
Sodium carbonate, anhy	do	48.0
Potassium bromide	do	1.5
Water to	liter	1

(*b*) Washed

(*c*) Re-exposed to light

(*d*) Developed in a mixture of equal parts of the following solutions to which was added aque-

ous ammonium hydroxide (0.92 0 s. g.) equivalent to 2% by volume.

A. Sodium sulfite	grams	2
p-Amino-N-diethylaniline	do	4
Metol	do	0.6
Water to	liter	1
B. Sodium carbonate	grams	40
Water to	liter	1

(e) The silver and residual silver halides were removed as in Ex. 1.

Example 4

A film element (Fig. 1) comprising a gelatin subbed cellulose nitrate film base 1 is coated to form a layer 2 with a gelatin dispersion containing 1 part of 1-(m-stearylaminophenyl)-3-methyl - 5 - pyrazolone-o-benzaldehyde sulfonic acid dimer to 4 parts of gelatin to a thickness of about 4.0 μ. A negative silver iodo-bromide emulsion sensitized with thiopseudocyanine ethiodide is coated upon layer 2 to form a light sensitive layer 3 about 2.5 μ in thickness. The film is then (1) exposed to an object, (2) developed 3 minutes in a positive type metol-hydroquinone developer, (3) washed without fixing, (4) re-exposed to light, (5) developed in the following solution prepared by mixing equal parts of A and B:

	Parts
A. Sodium carbonate	20
Sodium sulfite	1
Water	500
B. p-Amino-N-diethylaniline	2
Water	483

(6) The silver images and residual silver halides are removed in a potassium ferricyanide hypo solution, then washed and dried. A magenta image sharp and uniform in color is formed solely in layer 2.

Example 5

A film element of the type set forth in Fig. 1 is prepared by coating onto a subbed cellulose nitrate film base a gelatin dispersion of 1 part of m-octadecyloxyphenol to 5.5 parts of gelatin. A thin coating of a gelatino silver chloride emulsion is superposed thereon. The film is then (1) exposed to an object, (2) developed 3 minutes in a positive type metol-hydroquinone developer, (3) washed and (4) the reverse image without re-exposure is developed in an aqueous bath of the following composition:

p-Amino-N-diethylaniline	grams	2
Ammonium hydroxide, conc	cc	25
Sodium sulfite, anhy	grams	2
Water to	liter	1

prepared by adding the ammonia to a solution of the sodium sulfite and then adding the developing agent. Water was then added to make one liter. The images are removed with Farmer's reducer. A blue-green image remained in layer 2.

Example 6

A film element of the type set forth in Fig. 2 is prepared by coating a thin layer of a silver chlorobromide emulsion sensitized with thiopseudo cyanine ethiodide on a cellulose acetate film base, next a thin layer of a gelatin dispersion containing 1 part of 2-stearoylamino-5-naphthol-7-sulfonic acid per 7.5 parts of gelatin. The element is

(1) Exposed to a blue-green object.
(2) Developed in an ordinary developer.
(3) Washed.
(4) Developed without re-exposure in an aqueous bath of the following composition:

p-Aminodiethylaniline	grams	2
Piperidine	cc	25
Sodium sulfite, anhy	grams	2
Water to	liter	1

A blue-green image of good strength which is sharp and uniform in color results.

Example 7

A film element (Fig. 3) comprising a cellulose nitrate base 1 bearing a color-forming layer 2 prepared by coating thereon a gelatin dispersion of 1 part of salicyladelhyde phthalaldehydic acid acetal of polyvinyl alcohol dispersed in about 5.3 parts of gelatin to a thickness of 5.0 μ. A clear gelatin layer 4 is then coated on layer 2 to a thickness of about 2.0 μ. Next is coated a positive type silver iodobromide gelatin emulsion to a thickness of about 4.0 μ.

The film element is exposed and processed after the manner set forth in Example 1, except that a developer solution prepared by mixing equal parts of A and B was used:

A. Sodium sulfite	grams	2
p-Amino-N-diethylaniline	do	4
Metol	do	0.6
Water to	liter	1
B. Sodium carbonate	grams	40
Water to	liter	1

whereupon a blue-green image is formed. It is of good strength, uniform in color and microscopic examination shows the dye remains in the layer next to the base.

Example 8

A film element as shown in Fig. 3 is made after the manner set forth in Example 7, but substituting a gelatin dispersion containing 1 part of 1-(m-stearylaminophenylphenyl)-3-methyl-5-pyrazolone per 4 parts of gelatin for coating layer 2.

The element is exposed to an object and then treated as follows:

(a) Developed in a metol-hydroquinone developer of the following formula

Metol	grams	1.4
Sodium sulfite, anhy	do	60.0
Hydroquinone	do	5.0
Sodium carbonate, anhy	do	48.0
Potassium bromide	do	1.5
Water to	liter	1

(b) Washed
(c) Re-exposed to light
(d) Developed in a mixture of equal parts of the following solutions to which was added aqueous ammonium hydroxide (0.92 0 s. g.) equivalent to 2% by volume.

A. Sodium sulfite	grams	2
p-Amino-N-diethylaniline	do	4
Metol	do	0.6
Water to	liter	1.0
B. Sodium carbonate	grams	40
Water to	liter	1

(e) Bleached in an alkaline potassium ferrocyanide solution

(f) Fixed in plain, 25% hypo, then washed and dried.

A reverse magenta colored dye image is formed. It is of good strength and color and sharp in detail. A microscopic examination reveals that the dye image remains wholly within layer 2. No color is formed in layers 4 or 3.

EXAMPLE 9

A film base, e. g. subbed nylon, is coated with layers after the manner set forth in Example 5, except that an equal amount of dibenzoylacetbenzidide is substituted for the color former thereof.

The film element is exposed by passing a white printing light through a blue color separation negative transparency. It is then processed in the following manner.

(1) Developed in an ordinary developer of the type set forth in Example 8.

(2) Washed.

(3) Developed without re-exposure in an eqeous bath of the following composition:

p-Aminodiethylaniline	grams	2
Hexamethylene diamine (54% solution)	cc	15
Sodium sulfite	grams	3
Water to	liter	1

(4) Washed and bleached in an alkaline potassium ferricyanide solution.

(5) Fixed in plain 25% hypo solution.

(6) Washed and dried.

A yellow image is formed solely in layer 2. It is uniform in color, sharp in detail and of good strength.

EXAMPLE 10

A cellulose nitrate film base 1 (Fig. 4) is coated with a color former having film forming characteristics from a 2% solution of 3,5-dichlorsalicylaldehyde-orthobenzaldehyde sulfonic acid acetal of polyvinyl alcohol in 1 part of dimethyl formamide, 3 parts ethyl alcohol and 1 part water, which is made neutral by adding a small amount of caustic soda, to form a layer 2' about 1.0 to 1.5 μ thick. Next is coated a layer of a silver bromide emulsion about 4.0 μ thick.

The element is exposed to an image developed in a color forming developer of the following composition:

p-Amino-N-diethyl aniline hydrochloride	grams	4
Sodium sulfite	do	3
Sodium carbonate	do	25
Water to	liter	1

The silver and silver salt are removed by a silver solvent which does not attack color images. Suitable solvents include Farmer's reducer, a solution of potassium ferricyanide, and potassium bromide followed by sodium thiosulfate.

A green dye image remains which upon microscopic examination is found to be solely in layer 2'.

EXAMPLE 11

A film element (Fig. 5) is made by coating a cellulose nitrate base 1 with a silver halide emulsion 3 after the manner set forth in Example 2. Upon this layer is coated a layer 2' after the manner set forth in Example 10 with the same color former.

The film is exposed to light and then processed as follows:

(a) Developed in an ordinary developer such as a glycin sodium carbonate developer.

(b) Washed and dried.

(c) (Developed without re-exposure in a solution of the following composition:

4,4'-diaminodiphenyl amine	grams	4
Hexamethylenediamine	do	10
Sodium sulfite	do	2
Water to	liter	1

(d) Washed.

(e) The silver images are removed with a potassium ferricyanide-hypo solution.

A green dye image of good strength and color is formed solely in the layer 2'.

EXAMPLE 12

A film element of the type set forth in Example 10 was made by substituting for the color former coating solution thereof a solution of symmetrical bis(m-(5-keto-3-pyrazyl-)phenyl) urea-formaldehyde resin in an alcohol water solution (equal proportions containing 0.1 part of NaOH per part of resin).

The resulting film element was exposed to light.

(1) Developed 3 minutes in a positive type Metol-hydroquinone developer.

(2) Washed and dried.

(3) Re-exposed to light.

(4) Developed in the following solution prepared by mixing equal parts of A and B:

		Parts
A.	Sodium carbonate	20
	Sodium sulfite	1
	Water	500
B.	p-Amino-N-diethylaniline	2
	Water	483

(5) The silver images are removed in a potassium ferricyanide hypo solution, then washed and dried.

A magenta dye image which was sharp and clear in detail and uniform in strength and color was formed in layer 2' only.

EXAMPLE 13

A film element having a cellulose acetate base was made in the manner described in Example 10 but a coating solution comprising 1 part of salicylaldehyde-phthaldehydric acid acetal of polyvinyl acetal (sodium salt solution) and 2 parts of polymethacrylamide dissolved in equal parts of water and alcohol was used.

It is then exposed and developed after the manner set forth in Example 12 whereupon a blue-green dye image is obtained.

EXAMPLE 14

A two color print film as shown in Fig. 6 is made as follows: A cellulose nitrate film base 1 is coated on one side with a gelatin dispersion of one part of a mixture of yellow and magenta immobile color formers per 4 parts of gelatin. The mixture comprises diacetoacet-tolidine sulfone-o-benzaldehyde sulfonic acid dimer, 1 part, and 8 parts of 1-(m-stearylaminophenyl)-3-methyl-5-pyrazolone-ortho sulfobenzaldehyde dimer, 8 parts to form a layer 2 about 4.0 μ in thickness. A layer 2' is coated on the other side of the base from a gelatin dispersion comprising 1 part of 1-octadecyl amino-5-naphthol and 6 parts of gelatin to a thickness of about 4.0 μ. A light sensitive gelatino silver iodo-bromide emulsion containing a sensitizing dye is coated on

each of layers 2 and 2' to form layers 3 and 3' respectively.

The film element is then exposed by printing from bipack separation negatives by white or colored light onto the emulsion layers. On layer 3 there is imposed a latent image by printing with a blue light from the front negative of a bipack. On layer 3' by printing in a similar manner there is imposed a latent image from the rear film (orange red record) of the bipack. Suitable printing procedures and apparatus for the printing of the just-described film are set forth in Brewster U. S. Patent 1,253,137.

The film is then processed as follows:

(*a*) Developed in a solution of the following composition:

p-Amino-N-diethylaniline hydrochloride_g__	24
Sodium sulfite (anhydrous)_____g__	13
Sodium carbonate_____g__	20
Metol _____g__	2
Water to_____liter__	1

(*b*) Washed.

(*c*) Fixed in plain hypo (25% solution) and rinsed.

(*d*) Bleached for 7 minutes in 3.5% aqueous solution of potassium ferricyanide.

(*e*) Fixed in a plain hypo solution, washed and dried.

A color picture is formed in indophenol and azomethine dyes which is uniform in color, of good strength and clear and sharp in detail. A microscopic examination shows that the images are retained in the same strata the color formers were originally in.

Example 15

A film element of the type shown in Fig. 7 is prepared by coating a gelatin solution containing a yellow screening dye on one side of a cellulose nitrate base to form a thin layer 6. Over the yellow layer is coated a gelatin dispersion of one part of a mixture of yellow and magenta immobile color formers per 4 parts of gelatin. The mixture comprises diacetoacet-tolidine sulfone-o-benzaldehyde sulfonic acid dimer, 1 part, and 8 parts of 1-(m-stearoylaminophenyl)-3-methyl-5-pyrazolone ortho sulfobenzaldehyde dimer to form a layer 2 about 4.0 μ in thickness. A layer 2' is coated on the other side of the base from a gelatin dispersion comprising 1 part of 1-octadecylamino-5-naphthol and 6 parts of gelatin to a thickness of about 4.0 μ.

A light sensitive gelatino silver bromide emulsion is coated on each of layers 2 and 2' to form layers 3 and 3' respectively.

Color separation negatives from a two color bipack are printed on to the above-described film element as follows:

On layer 3 there is imposed a latent image by printing with a blue light from the front negative (blue-green record) of a bipack on 3' from the rear negative.

The exposed film element is processed to color after the manner set forth in Example 14.

Example 15—A

A film element of the general type shown in Fig. 7 is prepared by coating a gelatin dispersion of comminute silver particles on one side of a cellulose nitrate base, forming a thin layer with a neutral absorption density of 1 to 3, (as measured on a Marten's photometer). Over this is coated a gelatin dispersion of 1 part of a mixture of immobile yellow and magenta color formers per 4 parts of gelatin. The color former mixture comprises N-N'-di-(acetoacet)-m-tolidine-6,6'-sulfone-benzaldehyde-o-sulfonic acid dimer, 1 part, and 8 parts of 1-(m-stearoylaminophenyl) - 3 -methyl-5-pyrazolone-benzaldehyde-o-sulfonic acid dimer and the layer is coated to about 4 μ in thickness. Over this is coated a layer comprising a blue light sensitive gelantine-silver iodobromide emulsion of about 5 μ thickness. On the opposite side of the base is coated a blue light sensitive gelatin-silver iodobromide emulsion coated to a thickness of 5 μ. Next is coated a thin layer from a dispersion which consists of 1 part blue-green color former salicylaldehyde-ortho sulfo benzaldehyde mixed acetal of polyvinyl alcohol (sodium salt solution) dispersed in 3 parts of gelatin and coated to a thickness of about 4 μ.

A similar element which has considerable utility can be made by mixing the comminute silver with the mixture of immobile yellow and magenta color formers and gelatin to form a single layer. Similar duplicoated film elements can be made by mixing comminute silver with a single color former.

The exposed film elements of Examples 15 and 15A are then treated as follows:

(*a*) Developed 10 minutes in a solution prepared by mixing equal parts of the following

	Parts
A. Sodium carbonate_____	20
Sodium sulfite_____	1
Water_____	500
B. p-Amino-N-diethylaniline_____	2
Water_____	483

(*b*) Washed.

(*c*) The silver images and residual silver salts are removed by treatment with alkaline ferricyanide solution followed by fixing in plain 25% aqueous sodium thiosulfate solution.

A colored transparency which reproduces the original scene is obtained. The dye images are clear and sharp in detail with no dilution of color. A microscopic section shows the dye images to be in a single strata.

Example 16

A film element as shown in Fig. 8 is made by coating a cellulose nitrate film base 1 with a red sensitive high contrast gelatino-silver bromide emulsion sensitized with 20 mg. per kg. of emulsion, of 3,3'-diethyl-9-methyl thiocarbocyanine iodide to a thickness of about 4.0μ. Upon this layer is coated a gelatin dispersion of 1 part of the yellow color former N-furoylacet-N'-benzoyl-acetbenzidide per 4 parts of gelatin to form a thin layer 7. On this layer is coated a gelatin dispersion of 1 part of the magenta color former 1-(m-stearoyl-amino phenyl)-3-methyl-5-pyrazolone and 4 parts of gelatin to form a thin layer 8. A blue sensitive gelatin silver bromide emulsion containing a soluble yellow screening dye, e. g. tartrazine is coated on layer 8 to form a thin light sensitive layer 9. On the reverse side of the base is coated a gelatin dispersion containing the blue-green color former salicylaldehyde-o-benzaldehyde sulfonic acid acetal of polyvinyl alcohol, 1 part per 4 parts of gelatin to form a thin layer 10. Upon layer 10 is coated a photographic emulsion containing a yellow filter dye of the same type used for layer 9 to form a thin layer 11.

The film element may be exposed to printing

light from color separation negatives as described in Example 14, and then processed as follows:

(1) Developed 10 minutes in a bath of the following composition made by mixing equal parts of

A. Sodium sulfite	grams	2
p-Amino-N-diethylaniline	do	4
Water to	liter	1
B. Sodium carbonate	grams	40
Water to	liter	1

(2) Bleached 7 minutes in a solution containing 3½% by weight of potassium ferricyanide and made alkaline with ammonium hydroxide or sodium carbonate.

(3) Washed.

(4) Treated in a 25% solution of ammonium thiosulfate.

(5) Washed for 15 minutes and dried.

A colored transparency which faithfully reproduces the original scene is obtained. Microscopic examination shows that the color images remain solely in the layers in which the respective color formers were originally placed.

Example 17

A film element as shown in Fig. 9 is prepared as follows. An aqueous gelatin dispersion containing 2% of the sodium salt of salicylaldehyde-o-sulfobenzaldehyde mixed acetal with polyvinyl alcohol, and 4.5% of gelatin by weight, is coated on cellulose acetate film base 1 to form a thin layer 12. A red sensitive, green-blind silver iodobromide gelatin emulsion containing 18 mgs. per kg. of emulsion of 3-ethyl-α-naphthselenocarbocyanine-3'-ethiodide is coated on layer 12 to form a light sensitive layer 13. A plain gelatin layer 14 is coated on layer 13 and next an aqueous gelatin dispersion containing 1% of the magenta color former 1-(m-stearoylamino-phenyl)-3-methyl-5-pyrazolone to form a thin layer 15. Upon this layer is coated a light sensitive layer 16 comprising an orthochromatic negative gelatin silver chloride emulsion containing 3,1'-diethyl-5-methyl-6'-methoxy benz thio-2'-cyanine iodide. Next is coated a blue light screening layer 17 from a 2% aqueous gelatin dispersion of 0.3% by weight 4-piperonylbutadienyl-α-pyridinium stearyl bromide. On layer 17 is coated a thin yellow color forming layer 18 from an aqueous solution of gelatin containing 3.5% of gelatin and 1% of di(acetoacet-)metatolidine-6,6'-sulfone. A blue sensitive gelatino-silver bromide emulsion is then coated to form a thin outer layer 19. A water soluble antihalation layer 20 composed of a water-soluble animal glue, stearic acid and nigrosine is applied on the opposite side of the support.

The film element is exposed to a natural color scene and then processed as follows:

1. Develop 10 minutes in an ordinary metol-hydroquinone positive developer.
2. Wash 10 minutes.
3. Reduce residual silver salts by treating for 15 minutes in a dye-generating reducer of the following formula:

Sodium sulfite, anhydrous	gram	1.0
p-Aminodiethyl aniline dihydrochloride	do	2.0
Hexamethylene diamine (40%) solution	cc	20
Water to	liter	1

4. Wash 10 minutes.
5. Bleach 7 minutes in a solution containing 3½% by weight of potassium ferricyanide and made alkaline with ammonium hydroxide or sodium carbonate.
6. Rinse.
7. Remove bleached silver in a 25% solution of hypo (crystalline sodium thiosulfate).
8. Wash 15 minutes and dry.

The color photograph resulting from the above process is of exceptional clarity and brilliancy. The saturation of dyes or dye densities is considerably greater than that obtained by known methods of processing. A modified film may be made by incorporating comminute silver in the color former layer by preparing comminute silver particles and incorporating them in the gelatin dispersion, which forms the bottom color former layer. Microscopic examination shows that the color images remain solely in the layers in which the color formers were originally placed.

Example 18

A film element as shown in Figure 10 was prepared in the same manner as Example 17 except that the red sensitive emulsion layer and blue-green color former layers were reversed. This element comprises a cellulose nitrate base 1, a red-sensitive silver halide emulsion layer 13, next a blue-green color former layer 12, next layers 14, 15, 16, 17, 18 and 19 identical with those of Example 17. A water soluble antihalation layer 20 was coated on the reverse side of base 1.

The film was exposed to an original color scene and processed after the manner set forth in Example 16.

A modified film may be made by first coating a comminute silver layer on one side of the base to serve as an antihalation layer. The remaining film is made as above by superposing the layers on the antihalation layer.

Example 19

A film element as shown in Fig. 11 was prepared after the manner set forth in Example 17 using the same color formers. This element eliminates gelatin separating layer between the blue-green and magenta color forming layers. It comprises a cellulose acetate base 1, a red sensitive silver halide emulsion layer 13, a blue-green color former layer 12, a magenta color former layer 15, an orthochromatic silver halide emulsion layer 16, a magenta color former layer 15' containing a yellow screening dye, a yellow color former layer 18 and a blue sensitive silver halide layer 19. A non-halation layer 20 is coated on the reverse side.

This film is exposed and developed to dye images after the manner set forth in Example 17.

Example 20

A film element of the type set forth in Example 16 is prepared in the same manner, but the following color formers were used in place of those described in that example.

Blue-green

1 part ethylene maleic anhydride-1-p-amino benzylamino-5-naphthol polymer dispersed in 4 parts gelatin.

Magenta

1 part 2-stearoylamino-5-naphthol-7-sulfonic acid dispersed in 6 parts gelatin.

Yellow

3-allyl salicylaldehyde-ortho sulfo benzaldehyde mixed acetal of polyvinyl alcohol. One part of this is dispersed in 3 parts gelatin.

This film was exposed with white light through a positive color transparency with white light or with appropriately colored light through separation positive films or to an original color scene and then developed in the following solution:

	Parts
A. Sodium carbonate	20
Sodium sulfite	1
Water	500
	Parts
B. p-phenylenediamine hydrochloride	2
Water	483

Mix equal parts of A and B.

After development (the developing solution of Example I may also be used), and washing, the film is placed in a diazo solution prepared as follows: 6.1 parts of dianisidine is dissolved in 125 parts of boiling 1 molar hydrochloric acid and cooled to 2–4° C., then 10 parts of 5 molar sodium nitrite solution is added at 2–4° C. After 5 minutes, the mixture is filtered and diluted with ice water to 4000 parts. After the film has been immersed in this solution for 30 seconds, it is removed and immediately placed in a solution containing 3 per cent by weight of ammonia which has been cooled to 5° C. After remaining in this solution for 30 seconds, it is removed and thoroughly washed. The film is next placed in a solution prepared by dissolving first 10 parts of copper sulfate in 90 parts of water and then adding 5 parts of potassium bromide and 5 parts of concentrated hydrochloric acid. When the silver image has been completely oxidized the film is removed, washed and fixed. The resulting film contains a full color positive in azo dyes.

Film elements of the structure set forth in Fig. 1 to 11 inclusive which contain color formers capable of forming quinoneimine or azomethine dyes and azo dyes may be processed in a similar manner to that set forth in Example 20. Suitable procedures are also set forth in Woodward application, Serial No. 335,416, filed May 15, 1940, now U. S. P. 2,297,732.

In the embodiment of the invention wherein no re-exposure to light is used, the dye forming solutions set forth in Meschter application, Serial No. 295,686, now U. S. P. 2,310,981, may be used with similar results.

In place of the specific immobile color formers set forth in the preceding examples may be substituted a large number of exceedingly diverse color formers. The types which are to be dispersed in gelatin or other similar colloid binding agents may be (1) substantive to the gelatin or binding agent, (2) soluble in aqueous alkaline liquids but fast to diffusion when present in emulsion layers, (3) colloidal in nature so that they cannot be extracted by simple extraction from the layer, (4) high molecular weight so that migration through the cellular structure of the binding agent is prevented, (5) highly insoluble, (6) film-forming. Substantivity can be strengthened by agents which have precipitating action, e. g. diphenyl guanidide, diphenyl biguanidide, etc.

The immobile dye intermediates or color formers in general contain two components, (1) a color forming dye coupling component or nucleus and a component group or nucleus which increases the molecular weight so that they become immobile in the water permeable colloid layers or (2) groups for imparting substantive character (which are of the same type as used in making dyestuffs substantive to cotton), (3) groups or structures which make it colloidal in character.

Suitable dyestuff components for color-forming development and azo reversal processes hereof which fall within one or more of the above types of immobile color formers include:

1. Higher aliphatic and cycloaliphatic derivatives of dye intermediates wherein the aliphatic radical such as an alkyl, alkoxy or long chain carboxylic acid acyl radicals contain a carbon chain of more than 8 carbon atoms and preferably at least 12 carbon atoms, such compounds including active methylene compounds such as aroyl- or acylacetanilides, phenylmethylpyrazolones, etc., higher aliphatic amides of phenolic compounds, and alpha- and beta-naphthols which preferably contain some solubilizing group such as carboxyl or sulfonic, which are characterized in that they have a reactive position capable of entering the coupling reactants but not necessarily an unoccupied position ortho or para to the phenolic hydroxyl group. Suitable compounds of the cycloaliphatic type are set forth in U. S. Patent 2,189,817.

2. Polyvinyl acetals of aromatic aldehydes which are capable of reacting with diazo compounds and the oxidation products of photographic color developers. The acetals are formed from polyvinyl alcohol or partially hydrolyzed polyvinyl esters and aromatic aldehydes which contain a phenolic hydroxyl, amino, alkyl-, cycloalkyl-, or aryl-substituted amino group including mixed groups of this type, which are further characterized in that they have a reactive position, but not necessarily unoccupied position, ortho or para to the mentioned groups or the aromatic aldehydes having an active methylene group. The preparation of suitable compounds of this type is set forth in Dorough & McQueen application, Serial No. 233,480, filed October 5, 1938, now U. S. P. 2,310,943.

3. Condensation products of phenols and naphthols or hydroxy aromatic carboxylic or sulfonic acids with difunctional resin forming reagents such as aldehydes and ketones, dimethylol derivatives of phenols, amides and amines and equivalent compounds. The preparation of suitable color formers of this type is described in McQueen application, Serial No. 261,794, filed March 14, 1939 now U. S. P. 2,323,481.
481.

4. Condensation products of amine-containing dye intermediates such as aminophenols, aminonaphthols, N-aminoalkyl- or aminoaryl-aminonaphthols, amine containing active methylene compounds such as amino aroyl- or acetyl- acetanilids, amino-phenylmethylpyrazolones or any of the preceding compounds containing solubilizing groups such as carbonyl or sulfonic, with polycarboxylic acids and their derivatives such as the anhydrides, esters, amides or halides. Such polymeric acids include the olefin-maleic anhydride interpolymers, polyacrylic acids and interpolymers of esters of olefin dicarboxylic acids with vinyl esters, olefins and styrene as described in U. S. Patent 1,945,307.

5. Immobile dye intermediates formed from N-mono and dialkylated or aralkylated 1,5- and 1,8-aminonaphthols containing in a side chain a group capable of further condensation such as amino, thio, carboxyl, formyl, etc., by condensing said compound with a suitable high molecular weight compound such as aliphatic acids or amines with more than 8 carbon atoms or poly-

meric materials such as polyvinyl alcohol or polymeric acids or derivatives as listed above in paragraph 4.

Suitable immobile dye intermediates of the above and other types which are useful for color development and azocoupling processes are disclosed in U. S. Patents 2,154,918, 2,166,181, 2,178,612, 2,179,228, 2,179,238, 2,179,239, 2,179,244, 2,186,045, 2,186,719, 2,186,734, 2,186,735, 2,186,736, 2,186,849, 2,140,540, 2,133,937, 2,200,924, etc. and may be substituted for the dye intermediates of the above examples in accordance with the teachings hereof.

The preferred developing agents which may be used in the dye coupling development steps hereof 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-methylaminoaniline, p-ethylaminoaniline, p-aminophenol, N,N-diethyl-o-phenylenediamine, chloro-p-phenylenediamine, 1,2,5-toluylenediamine, 2-amino-5-diethylaminotoluene, p-amino-N-phenylmorpholine, N-p-aminophenylpiperidine, N-methyl-N-hydroxyethyl-p-phenylenediamine, N-butyl-N-hydroxyethyl-p-phenylenediamine, 2-amino-5-(N-butyl-N-hydroxyethyl) aminotoluene, β-γ-dihydroxypropyl-p-phenylenediamine, etc. These aromatic amino-developing agents in the form of their organic or inorganic acid salts 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.

Further examples of developing agents that can be used in this process are—heterocyclic compounds containing benzene nuclei such as 1,2,3,4-tetrahydro-6-aminoquinoline, 1,2,3,4-tetrahydro-6-amino-quinoxyline, etc. (British patent 478,345); o-aminophenols and their substitution products (French Patent 806,649); N-hydroxyalkyl p-phenylenediamine (British Patent 460,580); halogenated p-aminophenols (French Patent 813,902); p-phenylenediamine derivatives containing solubilizing groups in the positive radical connected to the N atom (French Patent 822,269); di-N-hydroxyalkyl p-phenylenediamine derivatives (U. S. Patent 2,108,243), and α-aminoacetoacetic acid ethyl ester.

The diazo solutions used in preparing the azo dyes may be prepared from many primary amines other than those used in the above examples. Amines which are suitable for diazotizing and coupling to azo dyes are well known in the art (see Fierz-Davis "Kunstliche Organische Farbstaffe" and J. C. Cain "The Chemistry of the Diazo Compounds," pages 6–26). There are in general of the type RNH_2 where R is aromatic or a heterocyclic ring such as pyridine, pyrazolone, etc. The R may also be substituted with various groups such as halogen, alkyl, alkoxy, aryl, sulfonic, carboxyl, etc. In choosing the amine to be used there are in general two considerations to be observed, (1) the diazo compound must be sufficiently active to couple readily with the dye intermediate used at a relatively low temperature and in aqueous solution; (2) the diazo compound must be one which can be coupled to yield bright azo dyes with spectral characteristics suitable for use in three-color photography, that is, they must have fairly definite and sharp absorption bands. Thus, the most suitable amines are those containing halogen, alkoxy, nitro, carboxy, and sulfonic acid groups.

For successful operation of the azo reversal processes hereof, it is necessary to have diazonium compounds that will couple with three colorless components to yield the three subtractive primary colors, yellow, magenta and blue-green. Almost all diazotisable amines can be coupled with phenolic coupling components and active methylene compounds such as phenylmethylpyrazolone, acetoacetanilide and aroylacetanilides, etc., to yield greenish-yellow to orange-yellow azo dyes. The number of combinations that yield magenta dyes is greatly limited, since the coupling components to conform to the previously mentioned requirement must be substituted alpha naphthols, and only a limited number of diazonium compounds will condense with such compenents to form magenta colors. Thus, diazotized aniline derivatives yield a magenta color only when substituted in the ortho or para position with such groups as phenyl and nitro. Tetraazotized diamino compounds such as benzidine and diaminonaphthalene derivatives substituted with halogen, alkoxy, and sulfonic acid groups may also be used. In forming the blue-green azo color, the choice is further restricted since the best colorless coupling components which adhere to the previous qualifications are derivatives of 1,5 and 1,8-aminonaphthol in which the amino group is preferably secondary or tertiary, and must remain basic. The preferred diazotizable amines that can be used for forming all three colors therefore are substituted benzidine derivatives containing halogen, alkyl, nitro, carboxyl, alkoxy or sulfonic acid groups, and substituted para-nitroaniline derivatives containing the 2 position halogen, alkoxy, nitro, carboxyl or sulfonic acid groups which all give desirable properties to the diazo components and to the dyes.

The novel film elements hereof are not limited in their use to the formation of azo dye images by the processes set forth above and in Woodward, Serial No. 335,416, now U. S. P. 2,297,732 but may be processed in other manners as described below.

The novel film elements hereof may be color developed and azo coupled after the manner set forth in British Patent 503,824 which involves an elimination of the quinoneimine or azomethine images by bleaching, if necessary.

The elements may also be exposed, bleached to a silver salt image such as a silver ferrocyanide which are then reduced with an aromatic hydrazine, and subsequently the silver and silver salts are removed. The dye intermediate in this case acts as an azo coupling component which couples with the development products of the hydrazine to form azo dyes. Suitable dye intermediates and processes are described in Woodward and McQueen application, Serial No. 299,760, filed October 16, 1939.

While gelatin has been described as the binding or supporting agent in the majority of the examples, the invention is not limited to the use of this material. On the contrary, a large number of materials some of which are readily available can be substituted in similar amounts and coated in the above manners. Natural and synthetic materials such as gums, resins, cellulose derivatives, carbohydrate derivatives, etc. The materials in general must be substantially water insoluble but water permeable.

Suitable specific materials include polyvinyl

alcohols including partially hydrolyzed polyvinyl esters, e. g. polyvinyl chloride and polyvinyl acetate; modified with resins such as polyvinyl acetals so that they have the above recited properties. The acetals may be formed from acetaldehyde, propionaldehyde, isobutyraldehyde, benzaldehyde, etc., ketones, glyoxylic acid, etc., alkyd resins including the modified alkyd resins which are prepared from polyhydric alcohols, e. g. glycerol, ethylene glycol and higher glycols and polybasic acids, e. g. phthalic, maleic, succinic, etc. Higher fatty acids, e. g. stearic, palmitic, and oils such as castor oil, may be used as modifying agents. The alkyd resins described in McQueen application, Serial No. 276,718, filed May 31, 1939, now U. S. P. 2,290,289, may be used.

Condensation products of phenols, of naphthols, or of hydroxy aromatic carboxylic or sulfonic acids with bifunctional resin-forming reagents, for example, aldehydes and ketones, dimethylol derivatives of phenols, of amides, or of amines, and of equivalent compounds, may be used.

Condensation products of amine-containing dye intermediates, with polycarboxylic acids or with their derivatives such as the anhydrides, esters, halides, or amides may be used. Polymeric acids of this type and their derivatives include the polyvinyl ethers of hydroxy acids, olefin-maleic anhydride interpolymers, polyacrylic acid, polymeric olefin discarboxylic esters and interpolymers of esters of olefin dicarboxylic acids with vinyl esters and styrene as described in U. S. Patent 1,945,307.

The above and equivalent materials as previously indicated can be used as binding agents for the color yielding layers as well as the silver salt layers or intervening layers in each of the herein described constructions of film elements.

While only a few types of film constructions have been set forth above and illustrated in the drawings, it should be understood that the invention is not limited to those modifications. Thus, a film forming type of color former may be imposed directly on a base which may be subbed, next an intervening water permeable layer and finally a reducible silver salt layer, or these layers may be reversed. Similar arrangements can be made with the dye intermediates incorporated in a water permeable binder or support. If a plurality of color yielding units are embodied in a film element one or more of the color yielding layers may be composed of film forming dye intermediates and the other or others may be composed of dye intermediates dispersed in binding mediums which are water permeable.

In the case of monopacks, various arrangements as indicated above may be made. The layers may be arranged so that exposure is made through the base. Thus, the elements shown in Figs. 9, 10 and 11, may be reversed with the base on top instead of the bottom. This requires a reversal of coating steps.

Not only may monopacks be fabricated, but bi- and tri-packs embodying the above constructions may be made without departing from the spirit and scope of the invention.

While cellulose derivatives have been described in the majority of the examples, various other types of transparent, translucent as well as opaque supports may be used. Synthetic resins including acrylic and hydrocarbon substituted acrylic acid resins, meta-styrene resins, vinyl resins, e. g. vinyl chloride acetal, polyvinyl acetals, synthetic linear polyamides, glass, paper and many other materials may be used.

An important aspect of this invention is briefly illustrated in Example 15—A, and involves the use of comminute silver in an immobile dye intermediate layer of an element used for multicolor photography. This embodiment may be used in films which contain at least one color yielding unit on each side of a transparent base. However, the elements must be so constructed that a combined comminute silver color yielding layer is between two reducible silver salt layers. This arrangement is advantageous in that it prevents a printing light from affecting one or more other sensitive layers. The above arrangements are of particular importance in duplicoats. It not only saves one coating step but produces in certain cases a superior product than if light screening dyes are used.

Various types of reducible silver salts may be used in the light sensitive layers. Initially they are generally silver halide layers such as simple and mixed chloride, bromide and iodide emulsions, including sliver bromide, silver chloride, silver chloride-bromide, silver bromide-iodide, silver iodide, etc. or the type used in the more conventional film elements used for color forming development. They may contain the usual emulsion components such as desensitizing dyes, sensitizing dyes, e. g. cyanine, carbocyanine, pseudocyanine, merocyanine, cyazine, carbocyazine, etc. salts and bases; etc. These light sensitive emulsions after development to silver images may be bleached in the usual manner to form silver ferrocyanide images before color development or color formation.

The particular types of coating solutions used can be made up and coated in a manner similar to those which have been used in the manufacture of film elements containing immobile dye intermediates in emulsion layers. The immobile dye intermediates may be dispersed in the binding agents while in a finely divided state using dispersing agents if desired and/or alkalies. In many cases it is practical to dissolve the dye intermediate or color former in a 5 to 10% caustic alkali to form a soluble paste. This may be then diluted with about 5 parts of water and about 1 part of alcohol added to 5% aqueous gelatin and the excess alkali neutralized with a mineral acid such as hydrochloric. The usual photographic coating ingredients, spreading agents, e. g. glycerine, saponine, long chain alkyl sulfates, etc. may be employed. The concentration of the coating solution is adjusted to yield the desired thickness.

The usual types of subbing solutions may be used for anchoring the silver halide emulsion layers to the base and to adjacent color former or intervening layers. The usual emulsion subbing solutions may also be employed to anchor the dye intermediate or color former layers to adjacent layers which may be emulsion layers or intervening layers.

This invention has a number of advantages, an important one being that the natural sensitivity and artificial sensitization of the silver halide emulsion layers is not impaired. Many color formers which are readily available and form excellent quinoneimine, azomethine and azo dyes have a very deleterious effect on the speed of photographic emulsions and for this reason cannot be used. In many cases the contrast of the film is excessively depressed. However, such color formers become of value when used in accordance with the teachings of this invention.

Another important advantage resides in the improved stability of the resulting film elements. The methods employed for incorporating color formers in emulsions often lead to unstable films. When dispersion is made before contact is made with the sensitive layer, this defect is eliminated. Furthermore, some color formers give rise to fog because of their chemical structure, but may be safely employed by this invention.

A further advantage resides in the fact that a wider selection of optical sensitizers is permitted. Many of the most powerful sensitizers for the red and green regions may not be employed in emulsions containing color formers—sensitization to the longer wave lengths being partially or completely destroyed by the color former. This incompatibility is avoided by placing the color formers in adjacent layers.

The invention also provides the following production advantages:

(*a*) Color former dispersions may be prepared in advance of the coating schedule. They may be standardized for degree of dispersion, colloidal stability, and color forming strength. All these operations may be carried out in white light areas; darkroom conditions being unnecessary prior to the coating operation.

(*b*) The consumption of costly materials is reduced since the colloidal dispersions are relatively stable, thus permitting them to be reworked by re-melting the chilled and jelled dye-forming colloid. On the other hand, previous research has shown that the photographic stability of light sensitive emulsion—color former preparations is short-lived and the uncoated preparations deteriorate rapidly even under refrigerated storage conditions.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope hereof it is to be understood that I do not limit myself to the specific embodiments herein except as defined by the appended claims.

I claim:

1. A photographic element comprising a transparent base having superimposed on one side thereof in order a red sensitive silver halide emulsion layer, a gelatin layer containing an immobile blue green color former, a gelatin layer containing an immobile magenta color former, a green sensitive silver halide emulsion layer, a gelatin layer containing an immobile magenta color former and a yellow light screening dye, a gelatin layer containing an immobile yellow color former and a blue sensitive silver halide emulsion layer.

2. A photographic element comprising in the following order a red sensitive silver halide emulsion layer, a gelatin layer containing an immobile blue green color former, a gelatin layer containing an immobile magenta color former, a green sensitive silver halide emulsion layer, a gelatin layer containing an immobile magenta color former, a gelatin layer containing an immobile yellow color-former, a blue sensitive silver halide emulsion layer and a stratum containing a yellow filter dye interposed before the green sensitive and red sensitive silver halide layers and a transparent base on one side of said element.

3. A photographic element comprising a transparent base having superimposed on one side thereof in order a red sensitive silver halide emulsion layer, a gelatin layer containing an immobile blue green color former, a gelatin layer containing an immobile magenta color former, a green sensitive silver halide emulsion layer, a gelatin layer containing an immobile magenta color former and a yellow light screening dye, a gelatin layer containing an immobile yellow color former and a blue sensitive silver halide emulsion layer and a non-halation layer on the other side.

4. A photographic element having a plurality of layers in the following order: a red sensitive silver halide emulsion layer, a gelatin layer containing the sodium salt of salicylaldehyde-o-sulfobenzaldehyde mixed acetal of polyvinyl alcohol, a gelatin layer containing 1-(m-stearoylaminophenyl)-3-methyl-5-pyrazolone-benzaldehyde-o-sulfonic acid dimer, a green sensitive silver halide emulsion layer, a gelatin layer containing 1-(m-stearoylaminophenyl)-3-methyl-5-pyrazolone-benzaldehyde-o-sulfonic acid dimer, a gelatin layer containing N-furoylacet-N'-benzoylacetobenzidide, a blue sensitive silver halide emulsion layer, a stratum containing a yellow filter dye interposed before the green sensitive and red sensitive silver halide layers, and a transparent base on one side of said layers.

5. A photographic element having a plurality of layers in the following order: a red sensitive silver halide emulsion layer, a gelatin layer containing an ethylene maleic anhydride-1-p-amino-benzylamino-5-naphthol polymer, a gelatin layer containing 2-stearoyl-amino-5-naphthol-7-sulfonic acid, a green sensitive silver halide emulsion layer, a gelatin layer containing 2-stearoylamino-5-naphthol-7-sulfonic acid, a gelatin layer containing 3-allyl-salicylaldehyde-o-sulfobenzaldehyde mixed acetal of polyvinyl alcohol, a blue sensitive silver halide emulsion layer, a stratum containing a yellow filter dye interposed before the green sensitive and red sensitive silver halide layers, and a transparent base on one side of said layers.

6. A photographic element having a plurality of layers in the following order: a red sensitive silver halide emulsion layer, a gelatin layer containing m-octodecyloxyphenol, a gelatin layer containing 1-(m-stearoylaminophenyl)-3-methyl-5-pyrazolone-benzaldehyde-o-sulfonic acid dimer, a green sensitive silver halide emulsion layer, a gelatin layer containing 1-(m-stearoylaminophenyl)-3-methyl-5-pyrazolone-benzaldehyde-o-sulfonic acid dimer, a gelatin layer containing di(acetoacet)-metatolidine-6,6'-sulfone, a blue sensitive silver halide emulsion layer, a stratum containing a yellow filter dye interposed before the green sensitive and red sensitive silver halide layers, and a transparent base on one side of said layers.

CLAYTON F. A. WHITE.

CERTIFICATE OF CORRECTION.

Patent No. 2,350,380. June 6, 1944.

CLAYTON F. A. WHITE.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 8, second column, line 53, strike out the number and period "481."; page 9, second column, line 19, for "compenents" read --components--; page 11, second column, lines 57 and 58, claim 6, for "benzaldedye" read --benzaldehyde--; 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 8th day of August, A. D. 1944.

Leslie Frazer

(Seal) Acting Commissioner of Patents.