April 5, 1938. L. D. MANNES ET AL 2,113,329

COLOR PHOTOGRAPHY

Filed Feb. 27, 1935

Fig. 1.

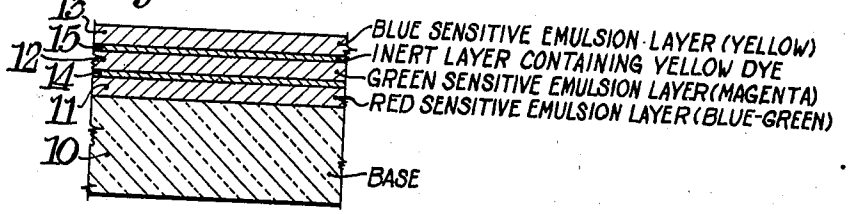


Fig. 2.

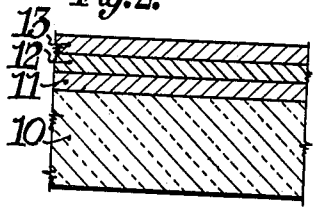


Fig. 3.

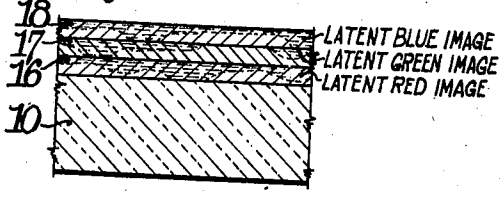


Fig. 4.

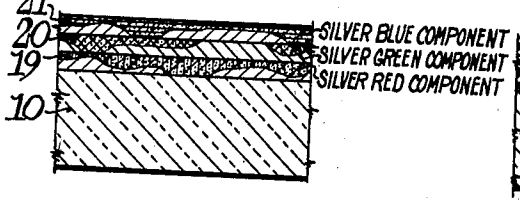


Fig. 5.

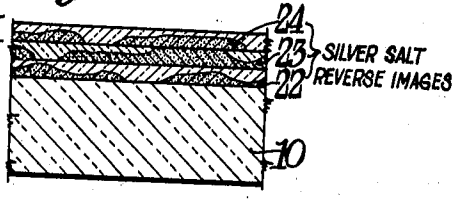


Fig. 6.

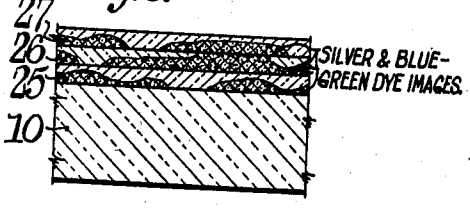
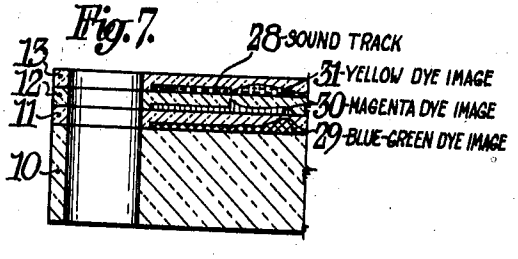


Fig. 7.



Inventors

Leopold D. Mannes & Leopold Godowsky, Jr.

By Newton M. Perrin
R. Frank Smith

Attorneys.

Patented Apr. 5, 1938

2,113,329

UNITED STATES PATENT OFFICE

2,113,329

COLOR PHOTOGRAPHY

Leopold D. Mannes and Leopold Godowsky, Jr., Rochester, N. Y., assignors, by mesne assignments, to Eastman Kodak Company, Jersey City, N. J., a corporation of New Jersey

Application February 27, 1935, Serial No. 8,516

18 Claims. (Cl. 95—2)

This invention relates to color photography and more particularly to a process in which a plurality of light-sensitive layers are treated to form a colored photographic record.

This application is a continuation-in-part of our application, Serial Number 634,182, filed September 21, 1932, matured into U. S. Patent No. 2,059,884, of November 3, 1936.

It is known in processes for producing colored photographs in which a plurality of layers of differently sensitized emulsions are treated to produce a colored photographic record by simultaneously exposing the layers, and then developing, fixing and coloring the resulting images in various ways. It has been proposed to dye the sensitized emulsion layer prior to exposure and later to remove the dye at the image or non-image portions. Processes have also been devised in which a dye-forming compound is mixed with the emulsion layer and a dye formed upon development. These processes all have numerous objectionable features, among which are the difficulties in processing and the inability of the user to obtain satisfactory colors.

An object of the present invention is to produce a satisfactorily colored photograph in two or more colors by simple and practical procedure. A further object is to produce a film adapted for taking pictures in three colors in which no coloring matter or color-forming substances is mixed with the emulsion prior to exposure. Other objects and advantages will be apparent from the following description.

These objects are accomplished by the following invention in which the colors are formed by a chemical coupling or dye formation, a dye being formed simultaneously and in situ with the development of the image.

Reference will be had to the accompanying drawing in which:

Fig. 1 is a sectional view of a film having three separate emulsion layers;

Fig. 2 is a modified form of film;

Figs. 3, 4, 5 and 6 are sectional views of the film illustrating the condition of the emulsion layers at various stages of the processing.

Fig. 7 is a sectional view of a finished film having a sound track recorded in three layers.

In practicing the invention we prefer to use a film of the type illustrated in Fig. 1 in which 10 is the usual type of transparent base such as cellulose nitrate or cellulose acetate. The sensitized silver halide emulsions are coated on one side of this base in three layers, the layer 11 coated next to the base being sensitive to red light, the intermediate layer 12 sensitive to green light and the top or outermost layer 13 sensitive to blue light. These layers are preferably separated by layers of inert material such as gelatin illustrated at 14 and 15. The layer 15 may contain a yellow dye in order to filter out blue light and prevent it from reaching the layers 11 and 12, which, while sensitive to red and green, are also sensitive to blue light. This yellow dye may, if desired, be incorporated in the outer blue sensitive layer 13.

The layers 11 and 12 are the usual silver halide emulsion layers sensitized to red and green light, respectively, with sensitizing dyes which are well known in the art. A suitable red sensitizing dye is naphthocyanol, and a suitable green sensitizing dye is erythrosin.

The process may be considered as divided into a series of units, each comprising a number of steps, and we will designate these as units A, B, and C.

This film is exposed in the usual way to form an image and since no filter is essential except that which is incorporated in the film itself, a shorter exposure may be made than with colored films heretofore used. However, a filter may be used to overcome errors in the color ratio, or to produce special effects.

In treating the film after exposure a reversal development may be used, thus forming a positive picture directly or the film may be developed as a negative and positives printed from it. An essential feature in the processing is a differential treatment of the layers by means of which the outer layer 13 may be treated without affecting layers 11 and 12 or the outer layers 12 and 13 may be treated without affecting layer 11. In order to aid in treating only the desired layers, the inert gelatine layers 14 and 15 are inserted between the sensitized layers to allow the operator some leeway. It has been found, however, that the differential treatment of the layers can be controlled with such a degree of accuracy that these inert layers are not absolutely necessary and in Fig. 2 a modification of the film is illustrated in which the sensitized emulsion layers are coated directly one on top of the other.

The process will first be described with reference to a reversal development. In using a film such as that illustrated, in which the base is coated with layers sensitive to three colors, the process steps may be divided into three separate units, at the end of each of which one of the layers is colored with the dye which it finally retains. Referring to Figs. 3 to 6 the steps of

unit "A" will now be described. The film after exposure contains latent images in each of the three emulsion layers, 11, 12 and 13. These are illustrated in Fig. 3, 16 being the latent image corresponding to the red of the object photographed, 17 the latent image corresponding to the green and 18 the latent image corresponding to the blue. The film is developed in an M—Q developer, forming silver images 19, 20 and 21 corresponding, respectively, to the red, green and blue of the object photographed.

A suitable developer has the formula:

Monomethyl p-aminophenol sulfate	g	5
Hydroquinone	g	10
Sodium sulfite	g	75
Sodium carbonate	g	30
Potassium thiocyanate	g	1¾
Potassium bromide	g	2½
Formalin (40%)	cc	2½
Water to	cc	1000

The film is next washed and then bleached in a bath which removes the silver but does not attack the silver halide present in each layer.

This bleach bath may have the following composition:

	Grams
Potassium permanganate (4% solution)	1
Sulfuric acid (20% solution)	1
Water	20

After the bleaching, the film is again washed, and then subjected to a clearing bath of sodium or potassium bisulfite or any other bath capable of removing from the film the manganese compounds or any other products that may have been formed in the bleaching operation. The customary bath for this purpose is a 2% solution of sodium bisulfite. The film is again washed, and is then ready to be exposed. Each of these washing steps, as well as the clearing bath, is carried out at 70° F. for about 4 minutes. The bleach bath is kept at a slightly lower temperature, about 65° F.

The developer contains, in addition to the usual developer constituents, including a para-amino aniline as the developing agent, a coupling or dye-forming compound such as any of the hydroxy diphenyls described in my copending application, Serial No. 8,520, filed February 27, 1935, matured into U. S. Patent No. 2,039,730, of May 5, 1936.

A suitable developer is the following:

(a)	p-Amino diethyl aniline monohydrochloride	g	3
	Sodium sulfite	g	5
	Sodium carbonate	g	50
	Potassium thiocyanate	g	½
	Water to	cc	1000
(b)	m-Hydroxy diphenyl	g	2½
	Methyl alcohol	cc	100

(In use, b is added to a)

The treatment of the film in this developer results in the formation of a silver image and simultaneously with the formation of the silver image a blue-green dye is formed by a combination of the coupling component with the oxidation product of the developer. Since the oxidation product of the developer is formed only at the points in the gelatin layers at which the latent image is reduced to metallic silver, a dye is formed only at those points and the coloring, therefore, proceeds simultaneously and in situ with the development. The film, after this treatment, is illustrated at Fig. 6 and contains the three-layer images consisting of metallic silver and blue-green dye at 25, 26 and 27. The film is then fixed to remove any residual silver halide which may be present, washed, and thoroughly dried. This completes unit "A".

The first step of unit "B" is the de-coloring of the dye in the outer layers 12 and 13, and the re-conversion of the metallic silver in these layers to silver halide. This may be done by the use of a bleach bath consisting of a solution of quinone and concentrated hydrochloric acid containing a retardant such as glycerine and isopropyl alcohol to control the depth of penetration of the bleach.

Such a bath may have the composition:

Glycerine	cc	500
Iso-propyl alcohol	cc	1000
Water	cc	75
Quinone	g	5
Hydrochloric acid (conc.)	g	20

The film is treated in this bath for about four minutes at 72 to 74° F. or for a sufficient time to bleach the two outer layers. The film is then immediately immersed in a stop bath which may consist of a solution of sodium bicarbonate, isopropyl alcohol and glycerine. This neutralizes the action of the bleach bath and prevents it from bleaching the dye in the inner layer 11.

This film is treated in this bath for about one and one-half minutes at 70° F. The composition of the stop bath is:

Sodium bicarbonate	g	15
Iso-propyl alcohol	cc	1000
Glycerine	cc	1000
Water	cc	1000

The stop bath which will be used will depend, of course, upon the type of bleach bath used, an alkaline stop bath being used to neutralize the action of the acid bleach bath. The dye contained in the outer layers 12 and 13 has now been de-colorized and the silver converted to silver chloride at the points at which there was a blue-green silver image at 26 and 27 in these layers. The film is then washed to insure removal of the de-colorized dye compounds and is then re-developed in a second color-forming developer which develops the silver chloride in the outer layers 12 and 13 to metallic silver and forms a magenta dye at the points at which the silver is formed. Such a developer may contain as the color-forming component p-nitro phenyl aceto nitrile, which couples with the oxidation product of the developer.

The magenta developer may have the following composition:

(a)	2-amino 5-diethyl amino toluene hydrochloride	g	1
	Sodium sulfite	g	10
	Sodium carbonate	g	30
	Potassium thiocyanate	g	½
	Water to	cc	1000
(b)	p-Nitro phenyl aceto nitrile	g	¾
	Acetone	cc	20
	Iso-propyl alcohol	cc	100

(In use, b is added to a)

The film is now washed and dried. This completes unit "B", and the film now contains a blue-green image in the innermost layer 11 and magenta images in the layers 12 and 13.

As the first step in unit "C" the magenta dye contained in the outer layer 13 is bleached and the

silver re-converted to silver halide. The bath used for this purpose is similar to the bleach bath used in unit "B" although the treatment is for a shorter time, for example two minutes at 72 to 74° F. The action of this bath is terminated by a stop bath as in the case of unit "B" and the film again washed. The outer layer is then redeveloped in a yellow-forming color developer which develops the silver chloride in the outer layer 13 to metallic silver and forms a yellow dye at the points at which metallic silver is formed. A suitable yellow dye forming compound is 4-nitro acetoacetanilide, although other substituted aceto-acetanilides as well as yellow dye forming compounds may be used.

A suitable yellow developer is:

(a)	p-Amino dimethyl aniline sulfate_g__	1
	Sodium sulfite_____g__	2
	Sodium carbonate_____g__	30
	Water to_____cc__	1000
(b)	4-nitro acetoacetanilide_____g__	2½
	Iso-propyl alcohol_____cc__	100

(In use, b is added to a.)

The film now contains a blue-green image in the inner layer 11, a magenta image in the intermediate layer 12 and a yellow image in the outer layer 13, together with metallic silver in each of the layers. The metallic silver is removed in a suitable bath such as potassium ferricyanide solution, leaving the film as illustrated in Fig. 7 (where a sound track is included), the emulsion layers now containing blue-green image 29 in the inner layer, magenta image 30 in the intermediate layer, and yellow image 31 in the outer layer. The film is then washed and dried.

We have described our process employing a film in which the emulsion layers are sensitized, from the base to the outer surface, to red, green, and blue light, respectively. The emulsion layers need not, however, be coated on the film in this order. For example, the green sensitive emulsion might be coated next to the base.

If it is desired to produce a negative from which positives may be printed, the exposed film may be treated in various ways.

(1) The film is developed in an ordinary metol-hydroquinone type of developer which may have the same formula as that used for the first development in the reversal processing. The film is then fixed to remove undeveloped silver halide and the remaining silver bleached to silver halide, for example, in a hydrochloric acid oxidizing bleach bath. The film is then color developed in a blue-green color developer having the same formula as that referred to in the description of the reversal development process. This results in blue-green negative images in each of the three layers. The film is then processed as described above under units "B" and "C". The film then has negative blue-green, magenta, and yellow images in the three layers.

(2) Instead of developing in an ordinary developer, the negative images may be developed directly in a color forming developer. However, when using this method excessive exposure seems to be necessary. Therefore, the use of a normal black and white photographic developer for initial negative development is preferable, giving maximum effective speed in the camera. After this color development, the film is treated as described in units B and C above.

(3) The film containing the latent images may be developed directly in a black and white photographic developer, fixed and bleached in dilute potassium ferricyanide to convert the silver images to silver ferrocyanide. This method is substantially the same as that described under method (1) above, except that the silver images are bleached to silver ferricyanide rather than silver halide. This is sometimes desirable because the silver ferrocyanide produced is very easily reducible back to metallic silver. A suitable bleach for this purpose is:

Potassium ferricyanide_____grams__	10
Ammonia—28% solution_____cc__	10
Water to_____cc__	1000

The next step is the exposure and redevelopment of the bleached images in the color forming developer yielding insoluble monochrome dye images together with redeveloped silver. The images in the outer layers are then bleached and recolored as described above under units B and C. The outer images are preferably bleached to silver halide, although a ferricyanide bleach may be used together with an acid to decolorize the dye.

(4) An alternative ferricyanide method may be used and, while it involves more steps than method 3, it has the advantage of minimizing any tendency to harden the gelatin in the image portions and, therefore, facilitates the attainment of satisfactory balance between the emulsions throughout the useful density range. By this method, the film is developed, fixed, washed and bleached in potassium ferricyanide to convert the images in both layers. The film is then exposed and the top layer only redeveloped to silver by controlling the penetration of an energetic developer and arresting the development as soon as the desired depth is reached. This arresting action is attained by loading the developer solution with an arresting agent, such as sodium sulphate. The following developer may be used:

Hydroquinone _____grams__	12.5
Sodium sulfite_____do____	19
Potassium hydroxide_____do____	41
Sodium sulfate_____do____	200
Water to _____cc__	1000

The action of this developing bath is arrested by immediate immersion in a stop bath, kept at very low temperature, for example 0° C. to 5° C. Such a stop bath is

Sodium sulfite_____grams__	50
Glacial acetic acid_____cc__	30
Water to _____cc__	1000

These methods of controlling and arresting the action of a bath so as to restrict its effect to an upper stratum is the subject of co-pending application, Serial No. 8,517, filed February 27, 1935, matured into U. S. Patent No. 2,059,887 of November 3, 1936.

At this stage of the processing, the film contains a developable silver ferrocyanide image in the inner layer and metallic silver images in the outer layers. The film is immersed in a blue-green color forming developer and the image in the inner layer developed to silver and blue-green dye. The silver images in the outer layers are, of course, inert to the color forming developer. The silver images in the outer layers may then be bleached in a potassium ferricyanide bath, the diffusion being controlled in the manner described in our said co-pending application Serial No. 8,517, matured into U. S. Patent No. 2,059,887 of November 3, 1936, to prevent its action on the dye image in the inner layer. The silver ferrocyanide images in the

outer layers may then be color developed to a single color and the outer layer only bleached and recolored, or the outer layer only may be redeveloped to silver and the intermediate layer then color developed by controlled penetration, and the outer layer finally converted to a silver salt and color developed.

In the negative processing the dyes used in addition to having the property of being easily bleached in the chromic acid, or other bleach bath used, should have as sharp an absorption band as possible to afford an efficient printing image.

This invention may also be applied to the formation of sound tracks in which the sound track is made up of differently colored, superposed images and may be of the variable density or of the variable width type. The sound track may be restricted to one layer or superposed in two or more layers and may be formed by one or more dyes. The restriction of the sound track to one or two layers may be accomplished by controlling the spectral transmission of the light used for recording the sound track on the finished print, so that the track is recorded only on the layer or layers sensitive to light of the color used. It is possible to allow the sound track in the various layers to bleach and color develop along with the development of the picture portion, or the sound track may be formed of one color in one or more of the layers and the sound track portion of the film varnished before the film is treated in subsequent treatment baths in order to limit the sound track to a single color. Fig. 7 shows a multilayer film in which the base 10 carries the three emulsion layers 11, 12 and 13 in which an image is recorded and also having a sound track portion 28 having the sound recorded in three layers.

We have described our process as adapted to the formation of three color component images, since a better reproduction of color may be obtained in this way. It is apparent, however, that the process is also applicable to the formation of two color component images by treating two differentially sensitized emulsion layers by the methods described. Where two colors only are used, the emulsion layers are sensitized with suitable color separation dyes, such as blue-green and red-orange.

Various other modifications of the process may be used. Numerous color forming compounds are suitable, as well as various bleach and stop baths. The emulsion layers may be coated on a paper or other support as well as on the transparent films and plates described. Numerous other modifications and variations of the process not herein specifically described are available and we intend to be limited only as we are restricted by the appended claims.

What we claim is:

1. The process of producing a colored photographic record on a sensitive element having a plurality of superposed, differently sensitized silver halide layers, which comprises simultaneously forming latent images in the layers, the images being different color sensation records of a subject, simultaneously developing the latent images to metallic silver images, bleaching the images to remove the silver, exposing the sensitive element to light, redeveloping the images in a color-forming developer, selectively bleaching at least the outer layer and redeveloping said last mentioned layer in a second color-forming developer.

2. The process of producing a colored photographic record on a sensitive element having three superposed, differently sensitized silver halide layers, which comprises simultaneously forming latent images in the layers, the images being different color sensation records of a subject, simultaneously developing the latent images to metallic silver images, bleaching the images to remove the silver, exposing the sensitive element to light, redeveloping the images in a color-forming developer, selectively bleaching the two outer layers, redeveloping the two outer layers in a second color-forming developer, bleaching the outer layer and redeveloping it in a third color-forming developer.

3. The process of producing a colored photographic record on a sensitive element having a plurality of superposed, differently sensitized silver halide layers, which comprises simultaneously forming latent images in the layers, the images being different color sensation records of a subject, simultaneously developing the latent images to metallic silver images, bleaching the images to remove the silver, exposing the sensitive element to light, redeveloping the images in a color-forming developer in which a color is formed simultaneously and in situ with development of a silver image, selectively bleaching at least the outer layer and redeveloping said last mentioned layer in a second color forming developer.

4. The process of producing a colored photographic record on a sensitive element having a plurality of superposed, differently sensitized silver halide layers, which comprises simultaneously forming latent images in the layers, the images being different color sensation records of a subject, simultaneously developing the latent images to metallic silver images, bleaching the images to remove the silver, exposing the sensitive element to light, redeveloping the images in a color-forming developer in which a color is formed by chemical coupling of a color-forming compound present in the developer with an oxidation product of the developer, selectively bleaching at least the outer layer and redeveloping said last-mentioned layer in a second color-forming developer.

5. The process of producing a colored photographic record on a sensitive element having a plurality of superposed differently sensitized silver halide layers, which comprises simultaneously exposing from the same side to form latent images in the layers, the images being different color sensation records of a subject, simultaneously developing the latent images to metallic silver and dye images by means of a color-forming developer, fixing out the unexposed silver halide, selectively bleaching at least the outer layer and redeveloping said last mentioned layer in a color-forming developer.

6. The process of producing a colored photographic record on a sensitive element having a plurality of superposed differently sensitized silver halide layers which comprises simultaneously exposing from the same side to form latent images in the layers, the images being different color sensation records of a subject, simultaneously developing the latent images to metallic silver and dye images by means of a color-forming developer in which a color is formed by chemical coupling of a color-forming compound present in the developer with an oxidation product of

the developer, fixing out the unexposed silver halide, selectively bleaching at least the outer layer and redeveloping said last mentioned layer in a color-forming developer.

7. The process of producing a sound track on a sensitive element having a plurality of superposed differently sensitized, silver halide layers which comprises forming a latent image of the sound track in each layer, developing said latent images to metallic silver, bleaching the images to remove the silver, exposing the sensitive element to light, redeveloping the images in a color-forming developer, selectively bleaching at least the image in the outer layer, and redeveloping said last-mentioned layer in a second color-forming developer.

8. The process of producing a sound track on a sensitive element having a plurality of superposed, differently sensitized, silver halide layers which comprises forming a latent image of the sound track on the sound track portion of the film, developing said latent image to metallic silver and dye images in a color-forming developer, coating the sound track portion of the film with a material impervious to subsequent treatment baths, and processing the film to produce color component images in the remaining portions of the film.

9. The process of forming two color component images in registry in two different strata on the same side of a photographic support that comprises forming a color component latent image in each stratum by exposing the strata from the same side of the support, developing each latent image into a silver image by a process which includes also the development of a color image in the lower stratum, subjecting the element for a controlled time to a bleaching bath containing a retardant for the diffusion thereof whereby the effect of the bath is limited to the upper stratum and the image therein is transformed into a developable image, and developing said image into a color image of different color than the image in the lower stratum.

10. The process of forming two color component images in registry in two different strata on the same side of a photographic support that comprises forming a color component latent image in each stratum by exposing the strata from the same side of the support, developing each latent image into a silver image by a process which includes also the development of a color image in the lower stratum, subjecting the element for a controlled time to a bleaching bath containing a retardant for the diffusion thereof whereby the effect of the bath is limited to the upper stratum and the image therein is transformed into a developable image, and developing said image into a silver image and a color image of a different color than the image in the lower stratum, and removing the silver images from both layers, leaving differently colored images in the respective strata.

11. The process of forming two color component images in registry in two different strata on the same side of a photographic support that comprises forming a color component latent image in each stratum by exposing the strata from the same side of the support, transforming each latent image into a silver image by a process which includes also the development of a color image in the lower stratum, subjecting the element for a controlled time to a bleaching bath containing a retardant for the diffusion thereof whereby the effect of the bath is limited to the upper stratum and the image therein is transformed into a developable image, and developing said image into a color image of different color than the image in the lower stratum.

12. The method of making a color photograph that comprises forming two images of silver and dye in different strata on the same side of a support by exposing the strata from the same side of the support, bleaching only the outer image in a bath that transforms the silver into a developable salt and decolorizes the dye and then redeveloping in a single step the outer image only into an image of silver and of dye of different color from the first named dye.

13. The method of making a color photograph that comprises forming two images of silver and dye in different strata on the same side of a support by exposing the strata from the same side of the support, bleaching only the outer image in a bath that transforms the silver into a developable salt and decolorizes the dye and then redeveloping in a single step the outer image only into an image of silver and of dye of different color from the first named dye and then removing the silver from both images, leaving in the different strata dye images of different colors.

14. The process of forming two color component images in registry in two different strata on the same side of a photographic support that comprises forming a color component latent image in each stratum by exposing the strata from the same side of the support, transforming both latent images by a single process into images of metallic silver and of the same dye by color developing, bathing the outer image only in a bath that transforms the silver image into a metallic salt image and that removes the dye and then treating the metallic salt image to form an image complementary in color to the image in the inner stratum.

15. The method of making a color photograph in an element having sensitized material in layer form on one side of a support, that comprises forming two images of the same color in two different strata of said sensitized material by exposing the strata from the same side of the support, submitting said element to a bath that diffuses into said material and is capable of decolorizing said images, said bath including a retardant for the diffusion thereof, stopping the action of the bath when the outer image only has been decolorized and then coloring said outer image a different color than the lower layer.

16. The process of forming two color component images in registry in two different strata on the same side of a photographic support that comprises forming a color component latent image in each stratum by exposing the strata from the same side of the support, transforming both latent images by a common process into images of silver and of the same dye, bathing the outer image only in a bath that transforms the silver image into a metallic salt image and that removes the dye, said bath containing an inert substance that retards the penetration of the bath into the strata, and, when the outer image only has been affected by said bath, quickly submitting the photographic element to a bath that immediately arrests the action of the first named bath and then treating the metallic salt image to form an image complementary in color to the image in the lower stratum.

17. The process of producing a colored photographic record on a sensitive element having a plurality of superposed differently sensitized

silver halide layers, which comprises simultaneously forming latent images in the layers, the images being different color sensation records of a subject, simultaneously developing the latent images to metallic silver images, bleaching the images to remove the silver, exposing the sensitive element to light, redeveloping the images in a color-forming developer, selectively bleaching at least the outer layer to remove the dye and convert the image to silver chloride, and redeveloping said last-mentioned layer in a second color-forming developer.

18. The process of producing a colored photographic record on a sensitive element having a plurality of superposed differently sensitized silver halide layers, which comprises simultaneously exposing from the same side to form latent images in the layers, the images being different color sensation records of a subject, simultaneously developing the latent images to metallic silver and dye images by means of a color-forming developer, fixing out the unexposed silver halide, selectively bleaching at least the outer layer to remove the dye and convert the silver to silver chloride, and redeveloping said last-mentioned layer in a color-forming developer.

LEOPOLD D. MANNES.
LEOPOLD GODOWSKY, JR.