

PATENT SPECIFICATION

Application Date : June 15, 1934. No. 16013 / 35. 440,089

(Divided out of Application No. 17743 / 34 (440,032.)

Complete Specification Left : June 1, 1935.

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PROVISIONAL SPECIFICATION.

Improvements in and relating to Colour Photography.

We, KODAK LIMITED, a British Company, of Kodak House, Kingsway, London, W.C.2, do hereby declare the nature of this invention, which has been communicated to us by Eastman Kodak Company, a body corporate organised according to the laws of the State of New York, United States of America, of 343, State Street, Rochester, New York, United States of America, to be as follows:—

This invention relates to colour photographic processes and in particular to the production of colour photographic records, especially for colour motion pictures.

In the production of colour photographic records it is known to employ a photographic record element having a plurality of superimposed emulsion layers sensitised to different colours and to expose such an element so as to obtain images in the respective layers corresponding to the colour sensations to which the respective layers are sensitised. The images in the respective layers may then be processed to different colours and are so processed in the subtractive processes to substantially the minus colours corresponding to the colours to which the respective layers were sensitised. Such reversal of the colour is, for example, employed in Specification No. 245,198. After a negative record element is thus formed by exposing a multi-layer record element in a camera and processing it in this way it is usually necessary to print it upon a similarly constituted positive photographic element which, after processing gives a representation in substantially true colours.

According to the process of the present invention, however, a multi-layer photographic element having colour sensations recorded in the respective layers is subjected to a process involving reversal of the images in the layers and such reversed images are then processed to the minus colours corresponding to the colours to which the layers were sensitive.

The process of the present invention may be applied to a three layer photo-

graphic element, for example one in which the layers respectively contain records of the red, green and blue colour sensations and in which the reversed images are to be processed respectively to minus red (blue-green), minus green (magenta), and minus blue (yellow). Such a film, especially a motion picture film, may comprise a support carrying on one side one emulsion layer protected by a removable waterproof coating and on the other side two emulsion layers, of which three layers two are uncoloured and sensitized to red and green respectively, while the third is sensitive to blue but insensitive to red and green, and removable yellow light filter means arranged to subtract the blue component from light passing through the blue sensitive layer into the red and green sensitized layers. Thus the support may carry on one side the emulsion layer sensitive to blue and on the other side the two uncoloured layers sensitised to red and green respectively.

The light filter means may comprise a layer containing removable or bleachable yellow colouring matter such as tartrazine and this is situated between the layer sensitive to blue and the other layers. Where the layer sensitive to blue is a single coating on one side of the support the yellow-coloured filter layer may be next to the support and may be on either or both sides thereof. Alternatively a bleachable or removable yellow dye may be incorporated in the blue sensitive layer itself or in part of this layer.

Preferably, the green sensitized layer lies between the red sensitized layer and the support. By way of example a suitable three-layer film is constructed as follows. On one side of a support or carrier there is coated a bleachable yellow filter layer. Over this is coated a silver halide emulsion layer which is sensitive to blue but insensitive to red and green. Over this layer is coated a clear colourless waterproof strippable varnish. On the other side of the support there is coated a silver halide emulsion sensitized to green and over this there is superposed



- a silver halide emulsion sensitized to red. Between the green sensitized and red sensitized emulsions there may be provided a thin layer of clear gelatine which prevents wandering of the sensitising dyestuffs from one layer to another and facilitates differential treatment of the two layers. Over the red sensitized emulsion there may be coated a removable anti-halation backing. Such a film is exposed from the blue sensitive side so that the single layer retains a record of the blue colour component while the double layers retain records of the red and green colour components respectively.
- In greater detail the process of treating the preferred three-layer film hereinbefore described may comprise the following steps:
1. Remove the anti-halation layer if necessary (This layer may be such that it is ordinarily removed in the developing step which follows.)
 2. Develop the two layers in the ordinary way to produce silver images therein.
 3. Remove the silver from these images.
 4. Expose the two-layer side of the film to white light from which the blue sensitive layer on the other side of the support is protected by the yellow filter layer.
 5. Colour develop the two layers to minus green.
 6. Fix if this development has not been carried to completion.
 7. Bleach the outer red sensitized layer to convert the silver image therein to a silver salt image and to remove the dye.
 8. Expose the two-layer side of the film to white light as in step 4.
 9. Colour develop layer 7 to minus red fixing again if this development is not carried to completion.
 10. Strip the waterproof coating from the single layer on the other side of the support.
 11. Develop this single layer to produce an image in silver.
 12. Remove the silver from this image.
 13. Expose to white light.
 14. Colour develop the silver halide to minus blue.
 15. Fix if this development is not carried to completion.
 16. Remove any residual silver from all the layers.
- At any suitable stage after step 10 the yellow colouring matter in the filter layer beneath the blue sensitive layer is bleached or removed or both by any suitable known means.
- In the treatment of the superposed layers in the above description we have indicated a method which involves development of the images in both layers to the colour required in the lower layer. It is possible, however, to develop the upper layer only to produce a silver image therein and then to develop to colour the image in the lower layer whereafter the silver image in the upper layer only is bleached and the bleached image re-developed to the appropriate colour. Such a procedure is described in copending application No. 26084 33 (Serial No. 427,472) under Negative Processing by Method B.
- The result of the above operations is to convert the negative images in the three-layer film directly to positive images in minus colours so that the film is, in effect, a positive in substantially the correct colours corresponding to the object to which the film was exposed.
- In the above description it will be seen that the bleached or unexposed silver salt layers which have to be developed are subjected to the action of light. If desired, however, suitable known ingredients may be incorporated in the developing baths to render the silver salt reducible by the developer without such exposure to light.
- Dated this 31st day of May, 1935.
W. P. THOMPSON & CO.,
12, Church Street, Liverpool, 1,
Chartered Patent Agents.

COMPLETE SPECIFICATION.

Improvements in and relating to Colour Photography.

- We, KODAK LIMITED, a British Company, of Kodak House, Kingsway, London, W.C.2, do hereby declare the nature of this invention, which has been communicated to us by Eastman Kodak Company, of 343, State Street, Rochester, New York, United States of America, a company organised under the laws of the State of New York, United States of America, and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—
- This invention relates to colour photographic processes and in particular to the production of multicolour photographic

elements, especially for colour motion pictures.

In the production of multi-colour photographic elements it is known to employ a photographic element having a plurality of emulsion layers, sensitized to different colours, superimposed on the same side of a single support and to expose such an element so as to obtain images in the respective layers corresponding to the colour sensations to which the respective layers are sensitized. The images in the respective layers may then be processed to different colours and are so processed in the subtractive process to substantially the minus colours of the colours to which the respective layers were sensitized. Such reversal of the colour is, for example, employed in Specification 245,198. After a negative record element is thus formed by exposing a multi-layer sensitized element in a camera and processing it in this way it is usually necessary to print it upon a similarly constituted positive photographic element which, after processing, gives a representation in substantially true colours.

The object of the present invention is to provide new or improved methods by which a photographic sensitized element have a plurality of emulsion layers sensitized to different colours superimposed on a single support in after exposure in a camera, directly processed to natural colours. The new or improved methods according to the present invention present advantages over any hitherto proposed and known to us. In carrying out the present invention it is not necessary for instance, to employ any optical sensitizer which has the ability to retain its optical sensitizing power for a subsequent light exposure after the successive action of a photographic developer and of a chemical solvent for silver.

According to the present invention, there is provided a method for directly processing to a natural colour photograph a photographic element having on a single support at least three gelatino-silver halide emulsion layers distributed as between the rear and front sides of the support and respectively containing superimposed latent image records of different colour sensations substantially covering the whole of the visible spectrum according to which reversed silver salt images are produced in all of the layers and at least all of the reversed silver salt images on that side of the support which carries more than one layer are simultaneously rendered developable, preferably by exposure to light and thereafter the reversed silver salt image in each of the layers is processed to the minus colour of

the colour of which the image is a record. In selecting the appropriate shade of the minus colour regard must be had to the nature of the light to be used in projection.

The colour processing preferably employed is colour development. The expression "Colour development," when used herein, is intended to designate a process effected by developing a silver image with a developer containing a colour former, as described in patent specification No. 376,838. Such colour formers are organic compounds acting as couplers in connection with certain developers to form coloured compounds usually insoluble in water, together with the finely divided silver which is being formed by development. The colour compound formed may belong, for example, to the class of indophenols, indoanilines and indamines and remains colloiddally dispersed in the gelatine layer even when the silver has been removed. It is thus possible to produce by this means a substantially transparent coloured image in proportion to the extent and depth of the original silver image. The expression "Colour development" when used herein does not therefore include the known process in which colour formers are incorporated in the layers themselves.

The photographic element preferably has three gelatino-silver halide emulsion layers respectively containing latent image records of red, green and blue.

Preferably the photographic element has only one emulsion layer on one side of the support. It most suitably has two on one side and one on the other.

Various methods may be employed for producing coloured, preferably colour developed, reversed images in the layers. In carrying out the present invention in its preferred forms all the latent images are first simultaneously developed to silver, the silver is bleached out, and the remaining reversed silver halide images are simultaneously rendered developable by exposure to light.

Owing to probable variation of conditions of the original exposure in the camera the reversed silver salt images may not be of the correct density for the direct production of a satisfactory transparent colour photograph. The method of the present invention lends itself to controlled exposure to light of the reversed silver salt images rendering it practicable to obtain reversed images of the correct density for the obtaining of as substantially true and brilliant a colour picture as is possible with the colours employed. In re-exposing the reversed silver salt images to light the exposure can be proportioned to the

optical density of the element so that the subsequently developed images shall be of the correct density. This is accomplished by controlling the exposure to light of the sensitive silver salts which remain after the removal of the developed negative silver images, as set forth in our prior patent No. 176,357, this exposure being analogous to the printing of a positive from a negative.

Since the controlled exposure to light may require the fixing out of any undeveloped silver salt remaining after subsequent development it is convenient to employ a method of processing in which the reversed silver salt images are simultaneously developed in the dark and then fixed. The subsequent steps in the processing may then be carried out in the light.

The processing of a three-layer element may therefore be accomplished by simultaneously colour developing the reversed silver salt images in all the layers to the minus colour required in the lower of the two layers on one side of the support; then the colour developed images in the upper of the two layers on the one side of the support and in the single layer on the other side of the support can be bleached and decolourized to reversed silver salt images and then selectively processed to the minus colours required in these layers. Such selective processing may be accomplished by flotation methods in which one side only of the photographic element is subjected to the action of a colour developer. Alternatively it may be accomplished by colour developing both the reversed silver salt images produced by bleaching (after the first colour development of all the layers) to the minus colour required in the upper of the two layers on the one side of the support, then covering the two layer side with a waterproof coating, then decolourizing and bleaching the colour developed reversed image in the single layer on the other side of the support and finally colour developing this bleached reversed image to the appropriate minus colour.

The processing of an element having a single layer on one side of the support may also be accomplished by simultaneously colour developing the reversed silver salt images in all the layers to the minus colour required in this single layer, fixing if necessary and then covering this single layer with a waterproof coating; the colour developed reversed images in the layers on the other side of the support can then be decolourized and bleached to reversed silver salt images and then respectively processed to their appropriate minus colours, preferably by operations involving colour

development and controlled bleaching, e.g. in the case of two layers by colour developing the reversed silver salt images in both layers to the colour required in the lower layer, bleaching and decolourising the image in the upper layer only, and then colour developing the bleached silver salt reversed image in the upper layer.

In alternative methods of processing, this single layer may be initially protected by a waterproof coating so that the latent images in the layers on the other side of the support may first be processed to colour developed reversed images and then the waterproof coating may be removed and the latent image in the single layer processed to a colour developed reversed image, preferably by operations involving colour development and controlled bleaching e.g. in the case of two layers by colour developing the reversed silver salt images in both layers to the colour required in the lower layer, bleaching and decolourising the image in the upper layer only and then colour developing the bleached silver salt reversed image in the upper layer.

Since the layers are distributed as between the rear and front sides of the support this invention has the advantage that the layer or layers on the one side are separated from the layer or layers on the other side by a water impervious layer, namely the support. Hence the risk of contamination of the colours of such layers is reduced as compared with other multi-layer processes and one is enabled to keep the number of different processing steps to a minimum. A further advantage is that the film is especially useful in conjunction with taking and projection lenses which are not fully corrected, for example where the colour component images come to a focus in different planes, and the positions of the layers on each side of the support are chosen accordingly.

The invention may be applied to the processing of a film, especially a motion picture film, which comprises a support carrying on one side one emulsion layer sensitive to blue but not to red or green and on the other side two emulsion layers which are uncoloured and sensitized to red and green respectively, removable light filter means being arranged to subtract the blue component from light passing through the blue sensitive layer into the red and green sensitized layers. For this purpose a removable yellow light filter may be provided between the blue sensitive layer and the support. Alternatively or in addition a bleachable or removable yellow dye may be incorporated in the blue sensitive layer itself or in a part of this layer for the purpose of acting

as a filter for the other layer and also for the purpose of modifying the characteristics of the emulsion.

Thus the film may comprise a transparent support of the usual type, for example of cellulose acetate or of cellulose nitrate, on the rear side of which is coated a thin layer of red sensitized emulsion, a thin intermediate layer of clear uncoloured gelatine and a thin layer of green sensitized emulsion and on the front side of which is coated a layer of clear yellow coloured gelatine, and a thin layer of blue sensitive emulsion. If desired the blue sensitive emulsion may be covered with a transparent waterproof stripping varnish layer. Benzyl cellulose forms a suitable waterproof coating as it may be easily stripped from the emulsion surface when it is desired to process the blue sensitive layer. A suitable varnish for this purpose is:

	Benzyl cellulose	150 gm.
	Benzene	1550 cc.
25	Toluene	100 cc.
	Xylene	400 cc.

(the manufacture of a low viscosity benzyl cellulose suitable for this purpose is described in British patent specifications Nos. 327,714, 333,902 and 356,308.)

There may be coated on the green-sensitized emulsion layer, if desired, a removable anti-halation backing.

The green sensitized emulsion may comprise a layer of a thickness of the order of .0002 of an inch of a very rapid emulsion sensitized to the green region of the spectrum between 510 and 590 $\mu\mu$. The sensitivity should be sharply limited towards 600 $\mu\mu$. Suitable sensitizers adapted to this are well known and erythrosin may be mentioned as suitable. The red sensitized emulsion is of the same order of thickness and is a rapid emulsion sensitized in the region from 600 to 700 $\mu\mu$, preferably with a maximum near 650 $\mu\mu$. It is preferably relatively insensitive to light of wave lengths around 520 to 530 $\mu\mu$. Sensitizers suitable for this purpose are also well known and naphtho-cyanol may be mentioned as an example. It is desirable for the upper layer to be more dilute as regards its content of silver halide so as to give greater transparency, less density, less tendency to exhaust the developer diffusing through it, and less tendency to harden the gelatine where the image develops.

The intermediate layer of clear gelatine and the yellow filter layer may be from 1 to 3 ten thousandths of an inch in thickness or less and the amount of yellow dye incorporated in the filter layer will generally be not more than between 0.25 m.gm. to 2 m.gm. per square centi-

meter, the exact amount depending upon the strength of the dye chosen and the efficiency of the filtering required. Suitable dyes are, for example, tartrazine (about 0.25 to 0.5 m.gm. per square cm.) which is removable or decolourized in water or the processing baths, quinoline yellow (about 1 m.gm. per square cm.) or brilliant yellow (about 0.5 m.gm. to 1 m.gm. per square cm.). When using such dyes as tartrazine, for example, which tend to diffuse into the adjacent layers, a further clear gelatine layer may be coated between the emulsion layer and the filter layer.

The layer of clear uncoloured gelatine between the green sensitized layer and the red sensitized layer prevents wandering of the sensitizing dyestuffs and facilitates differential processing of the layers. It must be clear enough to permit adequate exposure of the layer therebeyond and may, if desired, be suitably coloured to serve as a filter for the light falling on the layer therebeyond; e.g. it may contain a bleachable or removable red or green dyestuff according to the sensitivity of the layer therebeyond.

Alternatively the red or green sensitized layer may be placed on the rear end the green or red sensitized layer on the front with the blue sensitized layer above the layer on the front, suitable yellow filter means being provided in the manner indicated.

The silver halide employed in all the emulsion layers may be silver bromide and rapid emulsions should be used.

The thin layer of clear gelatine which is preferably present between two emulsion layers on the one side of the support facilitates the differential treatment of the images in the respective layers by allowing some leeway in controlling the penetration of the processing baths.

The film described above to which no claim is made in this application is exposed in the usual way from the front (so that the light falls first on the blue sensitive layer) to form latent images in the respective layers corresponding to the blue, green and red colour sensations, and since no filter is essential except that which is incorporated in the film itself, a shorter exposure may be made than with coloured films heretofore used. However, a filter may be used to overcome errors in the colour ratio, or to produce special effects.

The methods of processing, according to the present invention, will first be described in greater detail, by way of example, as applied to a film which is not provided initially with a waterproof varnish coating, and in which the blue sen-

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sitive layer is on the front side while the green and red sensitized layers are on the rear side the green sensitized layer being uppermost.

5 The anti-halation layer is removed if necessary. This layer may be such that it is ordinarily removed in the first of the steps which follow.

10 The film may first be treated to harden the gelatine slightly, e.g. by slightly tanning it, for the purpose of withstanding any alkali employed in the subsequent treatment. The film is then developed in the dark in an ordinary developer forming silver images in all the layers.

A suitable developer has the formula:

	Monomethyl <i>p</i> -aminophenol sulphate	5 gm.
	Hydroquinone	10 gm.
20	Sodium sulphite	75 gm.
	Sodium carbonate	30 gm.
	Potassium thiocyanate	1.75 gm.
	Potassium bromide	2.5 gm.
	Formalin (40%)	2.5 cc.

25 The film is next washed and then submitted to the action of a bath known as a reversing bath which removes the silver but does not attack the silver halide present in each layer.

30 This reversing bath may have the following composition:

	Potassium permanganate (4% solution)	1 cc.
	Sulphuric acid (20% solution)	1 cc.
35	Water	20 cc.

After this step, the film is again washed, and then subjected to a clearing bath of sodium or potassium bisulphate or any other bath capable of removing from the film the manganese compounds or any other products that may have been formed in the reversal operation. The customary bath for this purpose is a 2% solution of sodium bisulphite. The film is again washed, and is then ready to be exposed. Each of these washing steps, as well as the clearing bath, is preferably carried out at 70° F. for about 4 minutes. The reversing bath is kept at a slightly lower temperature about 65° F. All the above operations following development are also carried out in the dark.

The film now contains reversed light sensitive silver salt images in all the layers which have to be processed to the minus colours of the colours to which the layers were sensitized. This is accomplished by simultaneously rendering the silver salt images in all of the layers developable and then differentially processing the layers. In such differential processing use is made of some of the features described and claimed in our co-pending application No. 427,518.

65 In the method now being described in

detail, by way of example, the reversed silver salt images in all the layers are exposed to white light, the duration of exposure being determined, if desired, by the density of the images as in producing reversed silver images. In carrying out the differential processing of the layers, use is made of the methods described and claimed in our co-pending applications Nos. 427,516 and 427,520. The silver salt images in all the layers are first colour developed in the dark to minus red. The developer may contain a para-amino aniline as the developing agent and a hydroxy diphenyl as a coupling or dye-forming compound but other developers and couplers are well known in the art and may be used. We make no claim herein to the use of a hydroxy diphenyl as a coupler in a colour developing process.

A suitable developer is the following:

(a)	<i>p</i> -amino diethyl aniline monohydrochloride	3 gm.
	Sodium sulphite	5 gm.
	Sodium carbonate	50 gm.
	Potassium thiocyanate	0.5 gm.
	Water to	1000 cc.
(b)	<i>m</i> -hydroxy diphenyl	2.5 gms.
	Methyl alcohol	100 cc.

(In use, b is added to a).

The treatment of the film in this developer results in the formation of silver images and simultaneously with the formation of the silver images a blue-green (minus red) 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 silver shaft is reduced to metallic silver, a dye is formed only at those points and the colouring, therefore, proceeds simultaneously and in situ with the development. The film, after this treatment, contains images in the two emulsion layers on the one side and in the emulsion layer on the other side consisting of metallic silver and minus red dye. The film is then fixed to remove any residual silver halide which may be present, washed, and thoroughly dried. This drying step is of great importance in facilitating the differential treatment which follows. Since the residual silver halide has been fixed out there is no necessity to carry out any of the subsequent steps in the dark. The silver halides formed in the subsequent processing are conveniently rendered developable by working in white light.

The first step in the differential treatment of the layers is the de-colouring of the dye in the outer of the two emulsion layers on one side of the support and in the single layer on the other side of the

support 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 hydrobromic acid containing a loading agent (retardant) such as glycerine and iso-propyl alcohol to control the depth of penetration of the bleach. No claim is made herein to the use of glycerine or iso-propyl alcohol as a loading agent in photographic processing baths. A chromic acid bleach bath may be used containing a high concentration of methanol, for example, to serve as a loading agent.

A suitable bath may have the composition:

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

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

The 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	15 gm.
	Iso-propyl alcohol	1000 cc.
	Glycerine	1000 cc.
40	Water	1000 cc.

The stop bath which will be used will depend, of course, upon the type of bleach bath used, an alkaline stop both being used to neutralize the action of an acid bleach bath and a reducing agent, such as sodium bisulphite, being used to arrest the action of an oxidizing bleach bath. The dye contained in the outer emulsion layers upon which the bleach has acted has now been de-colourized and the silver converted to silver bromide at the points at which there was a minus red plus silver image in these layers. The film is then washed to insure removal of the de-colourized dye-compounds and is then developed in a second colour-forming developer which develops the silver bromide in the outer emulsion layer on the one side of the support and in the single emulsion layer on the other side to metallic silver and forms a minus green dye at the points at which the silver is formed. Such a developer may contain as the colour-forming component *p*-nitro phenyl aceto nitrile, which couples with

the oxidation product of the developer. Other well-known couplers can be used.

The minus green developer may have the following composition:

(a)	2-amino 5-diethyl amino toluene hydrochloride	1 gm.	70-
	Sodium sulphite	10 gm.	
	Sodium carbonate	30 gm.	
	Potassium thiocyanate	0.5 gm.	
	Water to	1000 cc.	75
(b)	<i>p</i> -nitro phenyl aceto nitrile	0.75 gm.	
	Acetone	20 cc.	
	Iso-propyl alcohol	100 cc.	
	(In use, b is added to a).		80

The film is now washed and dried.

The potassium thiocyanate used in this and the preceding developing formulæ is not essential but serves to increase the reduction potential of the developer. No claim is made to this in the present application.

The reversed images in the two layers on the same side of the support have now been developed to the appropriate minus colours. These two layers are now covered with a temporary waterproof stripping varnish which may be of benzyl cellulose such as the composition previously given. These two layers being now protected from the aqueous processing baths, the colour developed reversed image in the single layer on the other side of the support may be bleached and the silver reconverted to silver halide by treating the elements with a bleach bath, no control now being necessary. The single layer is then redeveloped in a minus blue colour developer which develops the silver bromide in the single layer to metallic silver and forms a yellow (minus blue) dye at the points at which metallic silver is formed. A suitable minus blue dye forming compound is 4-nitro-acetoacetanilide, although other substituted aceto-acetanilides or other well-known yellow dye forming compounds may be used. We make no claim herein to the use of substituted aceto-acetanilides as couplers in colour developing processes.

A suitable minus blue developer is:—

(a)	<i>p</i> -amino dimethyl aniline sulphate	1 gm.	
	Sodium sulphite	2 gm.	120
	Sodium carbonate	30 gm.	
	Water to	1000 cc.	
(b)	4-nitro acetoacetanilide	2.5 gm.	
	Iso-Propyl alcohol	100 cc.	
	(In use, b is added to a).		125-

The film now contains a blue-green (minus red) image in the lower emulsion layer on one side, a magenta (minus green) image in the upper emulsion layer on the same side and a yellow (minus blue)

- image in the single emulsion layer, on the other side, together with metallic silver in each of the layers. The waterproof varnish coating is now stripped off and the metallic silver is removed from all the layers in a suitable bath such as Farmer's solution, leaving dye images in the film. The film is then washed and dried and is a natural colour photograph. It has accurately superimposed clear transparent dye images containing no silver so that there is very little loss of light when the film is viewed as a transparency. Moreover, colour fringing is impossible.
- The process just described may be varied, after the stage of controlled bleaching, by redeveloping the reversed silver salt images in the outer of the two layers on the one side and the single layer on the other side of the support to minus blue. After washing and drying the single layer is coated with the waterproof stripping varnish. The upper of the two layers only is then again bleached by controlled penetration of a bleaching agent exactly as hereinbefore described. The waterproof stripping varnish is now removed from the single layer and the silver removed from all the layers leaving pure dye images.
- Another method of processing the photographic element containing reversed silver salt images in all the layers which have been rendered developable by controlled exposure to light is to develop the reversed images in all the layers in the dark to minus blue, then fix, cover the single layer on the one side with a stripable waterproof varnish coating and then bleach and selectively colour develop the bleached reversed images in the two layers on the other side of the support. This selective colour development may be accomplished by colour developing the bleached reversed images in both layers minus red, rebleaching the upper layer only as hereinbefore described and then colour developing the rebleached upper layer minus green. Alternatively the selective colour development may be accomplished by developing the image in the upper layer only to silver by controlling the penetration of an energetic developer and arresting the development as soon as the desired depth is reached. This control of penetration is facilitated by using a developer solution containing a high concentration of a loading agent, such as sodium sulphate. The following developer may be used:
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| Hydroquinone | 12.5 grams |
| Sodium Sulphite | 19 .. |
| Potassium Hydroxide | 41 .. |
| Sodium Sulphate | 200 .. |
| Water to | 1000 cc. |
- The action of this developing bath is arrested by immediate immersion of the photographic element in a stop bath, kept at very low temperature, for example 0° C. to 5° C. Such a stop bath is,
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| Sodium Sulphite | 50 grams |
| Glacial Acetic Acid | 30 cc. |
| Water to | 1000 cc. |
- At this stage of the processing, the film contains a developable silver salt image in the lower of the two layers on the one side of the support and a metallic silver image in the upper layer. The film is next immersed in a blue-green (minus red) colour forming developer and the image in the lower layer developed to silver and minus red dye. The silver image in the upper layer is of course, inert to the colour forming developer. The silver image in the upper layer may then be bleached in a potassium ferricyanide bath, the diffusion being controlled by the aid of loading agents and stop baths as described in our said co-pending application No. 427,518 to prevent its action on the colour developed image in the inner layer. The silver ferrocyanide image in the outer layer may then be colour developed to minus green.
- Alternatively the selective colour development of the two layers may be accomplished by causing a colour developer to act upon the bleached reversed image in one layer only at a time. For the treatment of the film hereinbefore described the reversed silver salt image in the upper layer only is colour developed by controlled penetration of a minus green colour developer. Such control may be facilitated by the presence in the colour developer of a loading agent and by the use of a stop bath.
- We make no claim herein to the use of a loading agent in a colour developer. The use of loading agents in processing baths is discussed in the specification of our application No. 427,518.
- The under layer is then colour developed to blue green (minus red). Before the step involving controlled penetration of a colour developer the film must be thoroughly dried.
- In such operations of selective colour development it may be desirable to add a substance, e.g. a thiocyanate, which increases the reduction potential of the developer but we make no claim to this in the present application.
- Whatever method of selective colour development is employed the final steps in the processing are the stripping of the waterproof layer and removal of the metallic silver from all the layers. After washing and drying the element is a three-colour photograph.

- If the first step in the colour processing does not involve simultaneous colour development of the reversed silver salt images in all the layers it may be desirable or necessary, in those cases where controlled exposure to light has left some silver salt in the layers substantially undevelopable, to develop in the dark the developable silver salt images in all the layers to silver and then fix, wash, rebleach and dry the element before processing it to colour. This procedure has the further advantage that the reversed images can be rebleached with ammoniacal ferricyanide to silver ferrocyanide which is readily reducible to silver even without exposure to light.
- In the methods of processing described above a strippable waterproof varnish layer is applied to one side of the element in order to protect the layer or layers on that side from the aqueous processing baths. It is possible, however, to dispense with the use of such a waterproof coating by employing known methods of flotation in which the film is floated on its side on a processing liquid which is thus kept out of contact with the other side.
- The film may be initially provided with a removable waterproof varnish coating for the purpose of enabling the two layer side to be first treated. The processing may then comprise the following steps:—
1. Remove the anti-halation layer if necessary.
 2. Develop the latent images in the two layers in the dark to silver images.
 3. Remove the silver from these two layers leaving reversed silver halide images.
 4. Expose the two-layer side of the film to white light from which the blue sensitive layer on the other side of the support is protected by a yellow filter layer.
 5. Colour develop the reversed silver halide images in the two layers in the dark to minus red.
 6. Fix if this development has not been carried to completion.
 7. Bleach the colour developed reversed image in the outer layer only to decolourise it and convert the silver to developable silver salt.
 8. Expose the two-layer side of the film to white light as in step 4.
 9. Colour develop the bleached reversed image in the upper layer in the dark to minus green, fixing again if this development is not carried to completion.
 10. Strip the waterproof coating from the single layer on the other side of the support.
 11. Develop the latent image in this layer to silver.
 12. Remove the silver from this layer leaving a reversed silver halide image.
 13. Expose to white light.
 14. Colour develop the reversed silver halide image to minus blue.
 15. Fix if this development is not carried to completion.
 16. Remove residual silver from all the layers.
- At any suitable stage after step 10 the yellow colouring matter in the filter layer beneath the blue sensitive layer is bleached or removed or both by suitable known means. It may be such that it is removed in the processing baths. The operations of silver developing, colour developing, bleaching and reversing may be carried out by the methods already described in detail.
- Whenever it is necessary, during the colour processing, to render the reversed images developable, this is preferably done by exposure to white light. It is possible however, in some cases to treat the element with known chemical reagents which will render the silver salts developable, for example as set forth in our prior patent No. 341,183. Such known reagents may be employed in some of the processing baths themselves.
- While it is preferable to produce coloured images by the operation of colour development as hereinbefore defined it is possible, in cases in which an image in one layer only exists as a silver image, and the images in the other layers have been colour developed to colour such an image by mordanting and dye toning.
- The invention is not limited to the treatment of the film described herein by way of example. It may be applied to the treatment of other photographic elements such as plates. The colour sensitization of the layers may be different from that given; thus the red and green sensitized layers may be interchanged.
- It will be apparent also that many of the methods herein described are applicable to photographic elements having more than three layers on the support, for example, three layers on one side and one on the other.
- Films treated by the process herein described may carry a sound track.
- Having now particularly described and ascertained the nature of the said invention and in what manner the same is to be performed, as communicated to us by our foreign correspondents, we declare that what we claim is:—
1. Method for directly processing to a natural colour photograph a photographic element having on a single support at

- least three gelatino-silver halide emulsion layers distributed as between the rear and front sides of the support and respectively containing superimposed latent image records of different colour sensations substantially covering the whole of the visible spectrum according to which reversed silver salt images are produced in all of the layers and at least all of the reversed silver salt images on that side of the support which carries more than one layer are simultaneously rendered developable, preferably by exposure to light and thereafter the reversed silver salt image in each of the layers is processed to the minus colour of the primary colour of which the image is a record.
2. The method as claimed in claim 1 in which the photographic element has three gelatino-silver halide emulsion layers respectively containing latent image records of red, green and blue.
3. Method as claimed in claim 1 in which all the latent images are first simultaneously developed to silver, the images are reversed, and the remaining reversed silver halide images are all simultaneously rendered developable by controlled exposure to light.
4. The method as claimed in claim 3 in which the photographic element has only one emulsion layer on one side of the support.
5. The method as claimed in claim 3 in which the photographic element has two emulsion layers on one side of the support and one on the other.
6. Method as claimed in any of the preceding claims in which the processing to minus colour is accomplished by colour development.
7. Method as claimed in claim 5 in which the exposed reversed silver salt images in all the layers are simultaneously colour developed to the minus colour required in the lower of the two layers on one side of the support, then the colour developed reversed images in the upper of these two layers and in the single layer on the other side of the support are bleached and decolourised to reversed silver salt images and finally these bleached and decolourised reversed silver salt images are selectively processed to the minus colours required.
8. Method as claimed in claim 7 in which the bleached and decolourised reversed silver salt images are selectively processed by colour developing them to the minus colour required in the upper of the two layers on the one side of the support, covering these two layers with a removable waterproof varnish coating, bleaching and decolourising the colour developed reversed image in the single layer on the other side of the support and then colour developing this bleached and decolourised reversed image to the minus colour required.
9. Method as claimed in claim 7 in which the bleached and decolourised reversed silver salt images are selectively processed to colour by colour developing them to the minus colour required in the single layer on the one side of the support, covering this single layer with a removable waterproof varnish coating, bleaching and decolourising the colour developed reversed image in the upper layer only of the two layers on the other side of the support and then colour developing this bleached and decolourised reversed image in the upper layer to the minus colour required.
10. Method as claimed in claim 4 or 5 in which the exposed reversed silver salt images in all the layers are simultaneously developed to the minus colour required in the single layer on the one side of the support whereafter this single layer is covered with a waterproof coating and the colour developed reversed images in the layers on the other side of the support are bleached and decolourised to reversed silver salt images and respectively processed to their appropriate minus colours.
11. Method as claimed in claim 4 or 5 in which after the reversed silver salt images have been produced in all the layers, a removable waterproof coating is applied to the single layer on one side of the support, the reversed silver salt images in the layers on the other side of the support are respectively processed to their appropriate minus colours and then the waterproof coating is removed from the single layer and the reversed silver salt image therein is processed to its appropriate minus colour.
12. Method as claimed in claim 5 in which the exposed reversed silver salt images in all the layers are simultaneously colour developed to the minus colour required in the single layer on one side of the support, whereafter this single layer is covered with a waterproof coating, the colour developed reversed images in the two layers on the other side of the support are bleached and decolourised to reversed silver salt images, these reversed silver salt images are simultaneously colour developed to the minus colour required in the lower layer, the colour developed reversed image in the upper layer only is decolourised and bleached to a reversed silver salt image and this a reversed silver salt image colour developed to the required minus colour.
13. Method as claimed in claim 5 in

which the exposed reversed silver salt images in all the layers are simultaneously colour developed to the minus colour required in the single layer on the one side of the support, whereafter this single layer is protected by a waterproof coating, the colour developed reversed images, two layers on the other side of the support are bleached and decolourised to reversed silver salt images, the reversed silver salt image in the upper layer only is developed to silver whereafter the reversed silver salt image in the lower layer is colour developed to its appropriate minus colour and then the silver image in the upper layer is bleached and colour developed to its appropriate minus colour.

14. Method as claimed in claim 2 in which the single layer on one side of the support is initially protected by a removable waterproof coating and the latent images in the two layers on the other side are first processed to reversed silver salt images which are then simultaneously rendered developable, preferably by exposure to light which will not affect the single layer on the other side, and processed to colour developed reversed images, whereafter the waterproof coating is removed and the latent image in the single layer is processed to a colour developed reversed image.

15. Method as claimed in claim 14 in which the latent images in the two layers on the same side of the support are simultaneously developed to silver, the silver images are reversed, the silver halide reversed images simultaneously colour developed to the minus colour required in the lower layer, the colour developed reversed image in the upper layer only decolourised and bleached to a reversed silver salt image and then this reversed silver salt image is colour developed before the waterproof coating is removed from the single layer on the other side of the support.

16. Methods for the production of multi-

colour photographs, substantially as described.

17. A sensitive element, especially a film, for colour photography having inseparably coated on a single support at least three gelatino-silver halide emulsion layers differentially sensitive to colours substantially covering the whole of the visible spectrum in which a layer sensitive to blue but insensitive to colours to which the other layers are sensitised is the sole light sensitive layer on one side of the support and in which between such layer sensitive to blue and the support is arranged a water-pervious decolourable yellow filter layer.

18. A sensitive element, especially a film, for colour photography as claimed in claim 17 in which the layers on the side of the support remote from the blue sensitive layer are respectively sensitised to red and green.

19. A sensitive element, especially a film for colour photography, as claimed in either of claims 17 or 18, in which the layer or layers of gelatino-silver halide emulsion on one side of the support are covered with a removable waterproof varnish.

20. A sensitive element, especially a film, for colour photography as claimed in any of claims 17 to 19 in which between adjacent layers of differentially colour sensitive emulsions is placed a thin layer of clear gelatine for the purpose indicated.

21. A sensitive element, especially a film, for colour photography, as claimed in any of claims 17 to 20 in which between the water pervious decolourable yellow filter layer and the adjacent blue sensitive layer is placed a thin layer of clear gelatine for the purpose indicated.

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