This reprint embodies the corrections allowed by the Assistant Comptroller acting for the Comptroller-General, dated the twentieth day of April, 1936, under Section 70 of the Patents and Designs Acts, 1907 to 1932.

PATENT SPECIFICATION

Application Date: June 15, 1934. No. 17743/34.
" " Nov. 10, 1934. No. 32441/34.

440,032

One Complete Specification Left: June 1, 1935.

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Accepted: Dec. 16, 1935.

PROVISIONAL SPECIFICATION
No. 17743 A.D. 1934.

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 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. Thus a two-layer photographic element in which the two layers are sensitised to complementary colours (for example the lower layer to green and the upper layer to red) may be treated, after exposure, by a process which involves reversal of the images and processing the reversed images to the minus colours corresponding to the complementary colours to which the respective layers were sensitised so as to produce directly in the element a substantially correct representation in colour of the object to which the element was exposed.

The invention also includes a film for colour photography, especially a motion picture film, comprising two uncoloured emulsion layers on a single support, one of which is sensitised to blue-green while the other is sensitised to orange-red and including removable yellow light filter means arranged to subtract the blue component from light passing through the blue-green sensitised layer into the orange sensitised layer. Such filter means may comprise a layer containing bleachable or removable colouring matter arranged between the two colour sensitised layers. Preferably the two layers are superposed on the support so that the layer sensitised to blue-green is uppermost and the layer sensitised to orange-red is undermost and the yellow filter is interposed between the two layers. The yellow filter may comprise a thin layer of transparent gelatine coloured with a suitable dyestuff which is adapted to be removed or destroyed in the subsequent processing.

The process of the present invention may also be applied to a three layer photographic element, for example one in which the layers respectively contain records of the red, green and blue colour sensations and in which the reversed

[*Price* 1/-]

images are to be processed respectively to minus red (blue-green), minus green (magenta), and minus blue (yellow).

Light filter means may be incorporated in the element comprising 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. 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 sensitised layer lies between the red sensitised layer and the support.

By way of example, a two-layer film may comprise a carrier having thereon superposed layers on the same side of the carrier which are sensitised to blue-green and orange respectively with an intermediate transparent layer containing a bleachable or removable yellow colouring matter. Such a film may be exposed in a camera so as to produce latent images in both layers of the colour sensation to which the layers are sensitised.

The processing of a two-layer film may comprise the following steps:

(1) Development to convert the latent images in both layers into silver images.

(2) Removal of the silver from the images.

(3) Exposure of the remaining silver halide for a suitable time to white light.

(4) Development of the exposed silver halide and fixation. The above steps may be accomplished by known reversal procedure after which the reversed or positive silver images are processed to orange and blue-green respectively, the blue-green image being formed in the layer which was sensitised to orange and *vice versa*. This processing, which involves differential treatment of the layers, may be accomplished by the operations described in copending application No. 26084/33 (Serial No. 427,472) under Negative Processing by Method A or Method B. Such processing broadly comprises bleaching the silver images, for example with potassium ferricyanide or a chromic acid bleach bath and then developing them by a process of colour development employing developers in conjunction with colour formers. Step 4 above may be omitted and the exposed silver halide differentially colour processed at once. Alternatively coloured images may be produced by converting the silver image into a mordant image and dyeing in the usual way.

At any suitable stage the yellow colouring matter in the filter layer is bleached or removed or both by any suitable known means.

The result of the above operations is to convert the negative images in the two-layer or 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 14th day of June, 1934.

W. P. THOMPSON & CO.,
12, Church Street, Liverpool, 1,
Chartered Patent Agents.

PROVISIONAL SPECIFICATION
No. 32441 A.D. 1934.

Improvements in or 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 to be as follows:—

This invention relates to improvements in or relating to colour photographic processes and in particular to methods of processing to colour a photographic element having at least three differentially colour sensitive layers on the same side of the support.

According to one feature of the present invention the process includes the selective colouring of images in at least three differentially colour sensitised layers on one side of a support while such layers are all on said support. According to a further feature of the invention the process of selective colouration of images in at least three differentially colour sensitised layers on one side of a support while such layers are all on said support comprises first processing all of the layers to the colour required in the lowermost layer, then bleaching the layers above the lowermost layer, then processing all the bleached layers to the colour required in the next lowermost layer, then rebleaching the layer or layers above the next lowermost layer, then processing the rebleached layers to the colour required in the next layer and so on, if required, until all the layers have been selectively

coloured; the processing is preferably accomplished by colour development of a developable image. The green sensitising dye incorporated in the green sensitised layer may be one which has a reddish colour thus serving at least partly as the light filter for the lower layer.

Alternatively a photographic element having at least three differentially colour sensitised layers on the same side of the support may be processed by first developing silver images in all the layers except the lowermost, then colour developing the image in the lowermost layer, then bleaching all the layers except the lowermost, then colour developing the next lowest and so on until all layers have been colour developed to different colours.

Finally the methods indicated above may be used in combination, employing for example the first indicated method for colouring the lower layer and the alternative method for colouring the other layers, or *vice versa*.

Other features of the invention will be apparent from the following description of preferred forms of the invention which will now be described by way of example.

A film is constructed which has on one side of the support five superimposed layers in the following order; a red sensitised rapid silver halide emulsion, a thin layer of unsensitised gelatine which may contain a small quantity of red dyestuff to act as a filter, a green sensitised rapid silver halide emulsion, a thin layer of unsensitised gelatine which preferably contains a yellow dyestuff to act as a filter and a blue sensitive silver halide emulsion which may contain a small quantity of yellow dyestuff for the purpose of modifying the characteristics of the emulsion but also serving in part as a filter for the layers beneath.

In processing the film described above, the latent images in all three layers are first developed to silver images by an energetic developer and the film then washed but not fixed and the silver removed from all the images. The film is then 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 now washed, exposed to light and developed with a minus red colour forming developer. This converts the silver salts in all the layers to images (which are reversed as to light and shade as compared with the first formed silver images) consisting of silver and blue-green dyestuff. Any undeveloped silver salts may then be fixed out. Preferably, however, the whole of the silver salts is completely reduced. The development must be correct as to the bottom layer.

After washing and drying, the colour in the top two layers is destroyed and the silver image coincidently bleached to a light sensitive silver salt image. This may be accomplished by controlled penetration of a bleaching agent. The control of penetration is facilitated by the employment in the bleach bath of a large quantity of loading agent, sufficient to retard the penetration of the bleaching agent through the upper two layers for a time permitting adequate bleaching to be accomplished. As loading agents sodium sulphate water-miscible organic liquids such as acetone, glycerol, other alcohols (especially methy or ethyl alcohol), sugars or other photographically inert water soluble substances which can retard the penetration of the photographic processing solution, for example by inhibiting the swelling of the gelatine or increasing the viscosity of the processing liquid. To arrest the action of the bleach bath a stop bath may be used e.g. a bath containing alkali such as ammonia for an acidic bleach or a bath containing hydroxylamine or hydrazine for a ferricyanide bleach.

The two top layers are next re-exposed and developed in a minus green colour forming developer and the film is washed and dried and the top layer only bleached to destroy the dye in the top layer and coincidently convert the silver in that layer to a light sensitive silver salt. The film is then washed, exposed and redeveloped in a minus blue (yellow) colour forming developer to convert the image in the top layer only to a dye plus silver image.

The film is finally treated to remove residual silver in all the layers, washed and dried.

It will be apparent that the process above described accomplishes reversal of the images in the layers and development to the colours complementary to the colours to which the respective layers were sensitised. The process may, however, be carried out by first developing the latent images initially produced to silver, fixing out all undeveloped silver salt, bleaching all the images to light sensitive silver salt and then proceeding by selective colour development and selective bleaching as described above.

It will be obvious that the invention is not limited to the colouring of images with the aid of colour-forming developers but other known methods of selectively colouring the images, either latent or otherwise, in the respective layers such as by mordanting may be employed.

Dated this 10th day of November, 1934.

W. P. THOMPSON & CO.,
Chartered & Registered Patent Agents,
12, Church Street, Liverpool, 1,

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 multi-colour 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 having a plurality of emulsion layers sensitized to different colours superimposed on the same side of a single support is, 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. Since all the layers are on the one side of the film such film is particularly useful for taking pictures in small sizes, e.g. cinematograph pictures, especially substandard sizes where the close proximity of the layers results in all the component images being sharply recorded when using a well corrected lens. Similar advantages accrue in projection.

According to the present invention, there is provided a method for directly processing to a natural colour photograph a photographic element having superimposed on the same side of a single support at least three gelatino-silver halide emulsion layers 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 all of such reversed silver salt images are simultaneously rendered developable preferably by exposure to light and thereafter the reversed silver salt image in each layer 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 if this is not true daylight.

In the specification of our application No. 427,516 we have described a method of colour photography in which a negative is produced upon a film having two emulsion layers sensitized to red and green respectively superimposed on the same side of a support. In the method there described the blue sensation is recorded in one area of the film in both layers and the red and green sensations are recorded separately in the two layers on another area of the film, the images in the two layers being afterwards processed to minus red and minus green respectively. It is stated that the finished negative may be printed by yellow light upon double coated positive material (which has similarly sensitized layers) whereafter the printed material may be put through an ordinary reversal treatment and then processed to minus colours. The

resulting processed element is a master negative for the process described and claimed in that application but is not a picture in natural colours. Even if the original negative containing the latent images were put through an ordinary reversal treatment and processed to the minus colours, the result would still not be a picture in natural colours, nor could it conveniently be projected or viewed to give a picture in natural colours by the subtractive principle.

In processing the reversed silver salt images to colour those in the two uppermost layers at least may be developed simultaneously. Thereafter less than all of the reversed images which have been simultaneously developed are bleached and selectively processed to colour.

The simultaneous development of the reversed images in two or more layers may be colour development to the colour required in the lowermost layer of those containing simultaneously redeveloped images. Less than all of the reversed images which have been simultaneously colour redeveloped are subsequently bleached and differentially processed to colour preferably by methods also involving colour development. It is preferable simultaneously to develop the images in all the layers after they have been rendered developable, the colour processing thereafter involving differential treatment of the developed reversed images in the respective layers.

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 satisfactorily 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. After development in the dark of all the exposed reversed images, preferably simultaneously, any silver salt which may have remained undeveloped can be removed by ordinary fixing agents after which the processing can be carried out in the light.

The selective colour processing of the developable reversed silver salt images in the layers may include selective development and may include selective colour development; thus it may include the step of submitting the photographic element containing the reversed silver salt images to a colour developer whose penetration is so controlled as to restrict the development to an upper layer or upper layers; or it may be accomplished by submitting the photographic element successively to colour developers whose penetration is so controlled as to restrict the development to an upper layer or upper layers. The selective colour processing may also be accomplished by first submitting the photographic element to an ordinary developer whose penetration is so controlled as to restrict its action to an upper layer (or upper layers), then colour developing the undeveloped reversed image in the remaining layer (or selectively colour developing the undeveloped reversed images in the remaining layers), then selectively bleaching the uncoloured silver image (or images) produced by the ordinary developer, then colour developing (or selectively colour developing) the bleached image (or images) and finally removing the silver from all the layers.

If the first step in the colour processing does not involve simultaneous development of the reversed silver salt images in all the layers it may be desirable or necessary, in these cases where controlled exposure to light has left some silver salt in one or more of 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.

For the production of a natural three-colour photograph the photographic element has three gelatino-silver halide emulsion layers which are resspectively sensitized to red, green and blue. The reversed silver salt images which are produced in these layers therefore represent the colour complement records of these colour components in the subject.

In processing the reversed silver salt images to colour those in the two uppermost layers at least may be developed simultaneously. Thereafter less than all of the reversed images which have been

simultaneously redeveloped are bleached. It is preferable simultaneously to redevelop the reversed silver salt images in all three layers and thereafter to bleach the redeveloped images in the upper two layers only.

An important feature of the invention consists in a method for directly processing to a natural colour photograph a photographic element having superimposed on the same side of a single support three gelatino-silver halide emulsion layers respectively containing latent image records of the red, green and blue colour sensations which includes producing developable reversed silver salt images in all of the layers, then submitting the element to a colour developer which develops all the images to the colour required in the lowermost emulsion layer, then fixing if necessary, then submitting the element to a bleaching agent whose penetration is so controlled as to restrict its action to the two upper emulsion layers the images in which are thereby recolourised and reconverted to silver salt, then submitting the element to a colour developer which develops the decolourised and reconverted silver salt images in both the upper layers to the colour required in the middle layer, then submitting the element to a bleaching agent whose penetration is so controlled as to restrict its action to the uppermost layer the image in which is thereby decolourised and reconverted to silver salt, then submitting the element to a colour developer which develops the decolourised and reconverted silver salt image in the uppermost layer to the colour required therein and finally removing the silver from all the layers leaving clear transparent dye images.

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 colloidally 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 manner of carrying out the present invention in practice will be described in greater detail, by way of example, with reference to the processing of a film comprising a transparent support of the usual type, for example of cellulose acetate or a cellulose nitrate, on which is coated a thin layer of red sensitized emulsion, a thin intermediate layer of clear uncoloured gelatine, a thin layer of green sensitized emulsion, an intermediate layer of clear yellow coloured gelatine and a thin layer of blue sensitive emulsion. It is essential that the yellow dye used for tinting the intermediate clear gelatine layer should permit the red and green light components to pass through with as little absorption as possible; on the other hand it should absorb the blue light component as completely a possible. It must, moreover, be decolourable or removable. These intermediate gelatine layers must be clear enough to permit adequate exposure of the sensitized layer therebeneath.

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 layers may be from 1 to 3 ten thousandths of an inch in thickness or less and the amount of yellow dye incorporated in the upper intermediate layer will generally be not more than between 0.25 m.gm. to 2 m.gm. per square centimeter, the exact amount depending upon the strength of the dye chosen and the effieciency 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 decolourised 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, further clear gelatine layers may be coated between the emulsion layers and the filter layer.

Between the green sensitized layer and the red sensitized layer there is, as indicated, a layer of clear uncoloured gelatine which prevents wandering of the sensitizing dyestuffs and facilitates differential processing of the layers. Such intermediate layer may, however, be suitably coloured if desired to serve as a filter for the light falling on the under-layer; e.g. it may contain a bleachable or removable red dyestuff if the underlayer is red-sensitized; or the green sensitizing dye incorporated in the green sensitized layer may be one which has a reddish colour thus serving in part at least as a light filter for the lower red-sensitized layer.

The blue sensitive silver halide emulsion may contain a small quantity of yellow dyestuff for the purpose of modifying the characteristics of the emulsion but also serving in part as a filter for the layers beneath.

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

The sensitive photographic element, e.g. the film described above, forms no part of the present invention which is concerned only with methods of directly processing it to a natural colour picture.

The thin layers of clear gelatine which are preferably present between the emulsion layers, as described above, facilitate 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 is exposed in the usual way to form latent images in the respective layers corresponding to the red, green and blue 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 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 with an ordinary developer forming silver images in all the layers.

A suitable developer has the formula:

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

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.

This reversing bath may have the following composition:

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

After this step, the film is again washed, and then subjected to a clearing bath of sodium or potassium bisulphite 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 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.

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 method described and claimed in our co-pending applications Nos. 427,516 and 427,520. The exposed 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 hydroxy diphenyl as a coupling or dye-forming compond, 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*) *p*-amino diethyl aniline monohydrochloride	3	gm.
Sodium sulphite	5	gm.
Sodium carbonate	50	gm.
Potassium thiocyanate	0.5	gm.
Water to	1000	cc.
(*b*) *m*-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 salt 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 all three emulsion layers 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 the light.

The first step in the differential treatment of the layers is the de-colouring of the dye in the two upper emulsion layers 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.
Water	75	cc.
Quinone	5	g.
Hydrobromic acid (conc.)	20	g.

The film is treated in this bath for a sufficient time to bleach the two upper layers which is about four 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 lower layer.

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

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 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 upper two emulsion layers 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 re-developed in a second colour-forming developer which develops the silver bromide in the upper two emulsion layers 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.
Sodium sulphite	10	gm.
Sodium carbonate	30	gm.
Potassium thiocyanate	0.5	gm.
Water to	1000	cc.
(*b*) *p*-nitro phenyl aceto nitrile	0.75	gm.
Acetone	20	cc.
Iso-propyl alcohol	100	cc.

(In use, *b* is added to *a*).

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 film is now washed and dried. It now contains a blue-green (minus red) image in the lowermost emulsion layer and magenta (minus green) images in the upper two emulsion layers. As before the drying step is of great importance in facilitating the differential treatment which follows.

As the next step the minus green dye contained in the upper emulsion layer is bleached and the silver reconverted to silver halide. The bath used for this purpose is the same as the bleach bath previously used for bleaching the upper two emulsion layers 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 bleaching of the two layers and the film again washed. The upper layer is then re-developed in a minus blue colour developer which develops the silver bromide in the upper 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-aceto-acetanilide, although other substituted acetoacetanilides or other well known yellow dye forming compounds may be used. We make no claim herein to the use of substituted acetoacetanilides as couplers in colour developing processes.

A suitable minus blue developer is:—

(*a*) *p* - amino dimethyl aniline sulphate -	1	gm.
Sodium sulphite - -	2	gm.
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*).

The film now contains a blue-green (minus red) image in the lower emulsion layer, a magenta (minus green) image in the intermediate emulsion layer and a yellow (minus blue) image in the upper emulsion layer, together with metallic silver in each of the layers. The metallic silver is removed 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.

An alternative method of differential treatment of the bleached out (reversed) developable images in the layers is to develop in the dark the images in the upper two layers only of the dried film 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:

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,

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 halide image in the lower layer and metallic silver images in the upper layers. If the film contains any silver salt in the upper two layers this may be removed by controlled penetration of a fixing agent. The film is next immersed still in the dark, 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 images in the upper layers are, of course, inert to the colour forming developer. Any silver salt remaining in the lower layer can be removed by fixing. The subsequent operations can then be carried out in the light. 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 No. 427,518 to prevent its action on the colour developed image in the lower layer. The silver ferrocyanide images thereby formed in the upper layers may then be colour developed to minus green, the film washed and dried, and the upper layer only bleached and recoloured minus blue, or the silver ferrocyanide image in the upper layer only may be re-developed to silver by controlled penetration of an energetic developer into the dried film and the intermediate layer may

then be colour developed to minus green and the upper layer finally converted to a silver salt and colour developed to minus blue.

Such a method of differential processing by controlled penetration of a silver developer and subsequent controlled penetration of a ferricyanide bleaching agent while it involves more steps than a method involving colour development and controlled penetration of an oxidising bleaching agent especially a chromic acid bleaching agent, 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. This method involves a sequence of steps similar to the sequence employed in the method described in Specification No. 376,838 for the differential treatment of superimposed latent images which have been simultaneously developed, fixed and bleached.

Another alternative method involving a sequence of steps similar to the sequence described in specification No. 376,838 for the differential treatment of superimposed latent images which have been simultaneously developed, fixed and bleached out may be employed in the differential treatment of reversed images. In this method the reversed developable silver salt images are all developed in the dark to silver and fixed if necessary whereafter the element is dried. The subsequent operations can then be carried out in white light. The silver image in the top layer only is bleached by controlled penetration of a ferricyanide bleaching agent. The bleached top layer is then colour developed with a yellow (minus blue) colour developer and the silver, which is deposited along with the dye, is removed from the colour developed top layer only by controlled penetration of a silver solvent. The two lower layers are then successively treated in similar manner.

In another method of differential treatment, the bleached out (reversed) developable images in all the layers are developed in the dark with a blue-green (minus red) colour developer and fixed if necessary. The subsequent operations can then be carried out in white light. The element is dried and the developed images in the upper two layers only are bleached, as hereinbefore described, the image in the top layer only developed to silver, the image in the intermediate layer colour developed with a magenta (minus green) colour developer, and finally the silver image in the top layer only bleached and then redeveloped with a yellow (minus blue) colour developer.

Another method of differential treatment of the layers is to subject the element to differential colour development. In such differential colour development the colour developer is permitted to act upon the imge in one layer only at a time. For the treatment of the film hereinbefore described the re-exposed reversed silver salt image in the upper layer only is colour developed in the dark by controlled penetration of a minus blue colour developer. Such control may be facilitated by the presence in the colour developer of a loading agent. 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. For the yellow (minus blue) colour developer for the image in the top layer we prefer to use the following formula in which the iso-propyl alcohol acts, in part at least, as a loading agent.

A	*p* - amino dimethyl aniline sulphate -	1	gm.
	Sodium sulphite - -	2	gm.
	Sodium carbonate -	30	gm.
	Water to - - -	1	litre
B	4 - nitro - aceto - acetanilide - - -	2.5	gm.
	Iso-propyl alcohol -	100	cc.

In use B is added to A.

Other known yellow dye forming compounds may be used.

The under layers are then successively colour developed in the dark, first by controlled penetration of a magenta (minus green) colour developer which preferably contains a loading agent to assist in confining its action to an intermediate layer, and finally by colour developing the bottom layer to blue green (minus red). Before each 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 invention.

It will be apparent that some of the methods hereinbefore described may be employed in combination with one another. Thus the re-exposed reversed image in the top layer only may be redeveloped in the dark to silver and the images in the remaining layers colour developed in the dark by the method involving controlled penetration of a colour

developer as just described. The film is then fixed and the subsequent operations can accordingly be carried out in white light. Thereafter the silver image in the top layer only may be bleached and the bleached image redeveloped with a colour developer.

It will be apparent also that in the alternative methods described above employing colour development the silver which is deposited along with the dye is removed at an appropriate stage by known silver solvents. Wherever possible, such removal of silver is accomplished after the images in all the layers have been colour developed.

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.

Whenever it is necessary, before and 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.

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 and to elements having three or more layers containing different colour sensation records in any order.

The emulsion layers may be coated on a paper or other support to enable the colour picture to be viewed by reflected light as well as on the transparent films and plates described.

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 superimposed on the same side of a single support at least three gelatino-silver halide emulsion layers 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 all of such reversed silver salt images are simultaneously rendered developable preferably by exposure to light and thereafter the reversed silver salt image in each layer 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 which respectively contain latent image records of red, green and blue.

3. Method as claimed in Claim 1 in which the reversed silver salt images in two adjacent layers at least are simultaneously developed.

4. Method as claimed in Claim 2 or 3, in which the reversed silver salt images in the two uppermost layers at least are simultaneously developed.

5. Method as claimed in Claim 3 or 4 in which less than all of the reversed images which have been simultaneously developed are subsequently bleached.

6. Method as claimed in Claim 1 or 2, in which the reversed silver salt images in all the layers are simultaneously developed whereafter the developed images in the upper two layers only are bleached.

7. Method as claimed in any of Claims 3 to 6, in which the simultaneous development is colour development to the colour required in the lowermost layer of those containing the simultaneously developed images.

8. Method as claimed in Claim 5 or Claim 6 in which the bleached reversed images are subsequently colour developed.

9. The method claimed in Claim 1 or 2, in which the reversed images which have all been simultaneously rendered developable and are to be processed to colour are selectively developed.

10. The method claimed in Claim 9 in which the selective development includes colour development.

11. The method claimed in Claim 10 in which the selective development includes the step of submitting the photographic element to a colour developer whose penetration is so controlled as to restrict the development to an upper layer or upper layers.

12. The method as claimed in Claim 9 in which the selective development is accomplished by submitting the photographic element successively to colour developers whose penetration is so controlled as to restrict their action to an upper layer or upper layers.

13. The method claimed in Claim 9 in

which the selective development is accomplished by first submitting the photographic element to an ordinary developer whose penetration is so controlled as to restrict its action to an upper layer (or upper layers, then colour developing the undeveloped reversed image in the remaining layer (or selectively colour developing the undeveloped reversed images in the remaining layers), then selectively bleaching the uncoloured silver image (or images), produced by the ordinary developer, then colour developing (or selectively colour developing) the bleached image (or images), and finally removing the silver from all the layers.

14. Method for directly processing to a natural colour photograph a photographic element having superimposed on the same side of a single support three gelatino-silver halide emulsion layers respectively containing latent image records of the red, green and blue colour sensations which includes producing developable reversed silver salt images in all of the layers, then submitting the element to a colour developer which develops all the images to the colour required in the lowermost emulsion layer, then fixing if necessary, then submitting the element to a bleaching agent whose penetration is so controlled as to restrict its action to the two upper emulsion layers the images in which are thereby decolourised and reconverted to silver salt, then submitting the element to a colour developer which develops the decolourised and reconverted silver salt images in both the upper layers to the colour required in the middle layer, then submitting the element to a bleaching agent whose penetration is so controlled as to restrict its action to the uppermost layer the image in which is thereby decolourised and reconverted to silver salt, then submitting the element to a colour developer which develops the decolourised and reconverted silver salt image in the uppermost layer to the colour required therein, and finally removing the silver from all the layers.

15. Method as claimed in any of the preceding claims in which the reversed silver salt images in all the layers are simultaneously rendered developable by controlled exposure to light.

16. Method for directly processing to a natural colour photograph a photographic element, substantially as described.

Dated this 31st day of May, 1935.

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