PATENT SPECIFICATION

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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 246,198. 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
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 pending application No. 26084/33 (Serial No. 427,473) 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 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.

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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 processed.
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 that is largely bleached out by 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 develop-
ing silver images in all the layers except 
the lowestmost, then colour developing the image in the lowestmost layer, then 
bleaching all the layers except the lower-
most, 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 above indicated method 
for colouring the lower layer and the alter-
native 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 sensi-
tised rapid silver halide emulsion, a thin 
layer of unsensitised gelatine which may 
contain a small quantity of red dye stuff to 
act as a filter, a green sensitised rapid 
silver halide emulsion, a thin layer of un-
sensitised gelatine which preferably con-
tains a yellow dye stuff to act as a filter 
and a blue sensitive silver halide emulsion 
which may contain a small quantity of 
yellow dye stuff for the purpose of modi-
fying 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 
enertic developer and the film then 
washed and fixed and the silver re-
moved 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 
ye stuff. Any undeveloped silver salts 
may then be fixed out. Preferably, how-
ever, the whole of the silver salts is com-
pletely 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 pene-
tration of a bleaching agent. The control 
of penetration is facilitated by the em-
ployment 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 process-
ing 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 ammonium for an acid 
bleich or a bath containing hydroxyl-
amine or hydroxylamine for a ferricyanide 
bleich. 
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 re-
developed 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.
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 349, 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 sensitiser which has the ability to retain its optical sensitising 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 suitable 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 gelatine-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 on 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 neutral white. In the specification of our application No. 437,516 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 printed negative may be printed by yellow light upon double coated positive material which has similarly sensitized layers where-after 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 conventionally 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 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 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. After development of 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 be accomplished by first submitting the photographic element to an ordinary developer whose penetration is so controlled as to restrict its action to a smaller 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, re-bleach and dry the element before processing it to colour. This procedure has the further advantage that the reversed images can be re-bleached with ammoniacal ferricyanide to silver ferrocyanide which is readily reducible to silver even without exposure to light.

For the production of a natural tricoloured photograph the photographic element has three gelatino-silver halide emulsion layers which are respectively 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 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 leaving clear transparent dye images.

The expression "Colour Development", when used herein, is intended to designate a process effecting a developing a silver image with a developer containing a colour former, as described in patent specification No. 376,893. 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 colloidal dispensed in the gelatine layer even when the silver has been removed therefrom. It is 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 at 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 590μ. The sensitivity should be sharply limited towards 600μ. 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 700μ, preferably with a maximum near 650μ. It is preferably relatively insensitive to light of wave lengths around 520 to 590μ. 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. g. m. per square centimeter, 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. g. m. per square cm.) which is removably 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.

10 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 an 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 under-layer 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.

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

20 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.

25 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 employed. 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 tangling 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 copending 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 copending applications Nos. 427,518 and 125,427,520. 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 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) 2-amino diethyl aniline monohydrochloride - 8 gm.
Sodium sulphite - 3 gm.
Sodium carbonate - 30 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 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 in 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 leading 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 leading 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. 70
Iso-propyl alcohol - - - 1000 cc. 73
Water - - - 73 cc.
Quinone - - - 5 g.
Hydrobromic acid (conc.) - 20 g.

The film is treated in this bath for a sufficient time to bleach the upper two 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 80 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. 90
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 bleaching 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 100 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 2-nitro phenyl acetone 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. 120
Sodium sulphite - - - 10 gm.
Sodium carbonate - - - 30 gm.
Potassium thiocyanate - - - 0.5 gm.
Water to - - - 1000 cc.
(b) p-nitro phenyl acetone 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 formulae 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-aetoacetanilide, 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 transparencies. 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 " 80
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 penetra
tion of a ferriyanide bleaching agent
while it involves more steps than a
method involving colour development and
controlled penetration of an oxidising
bleaching agent especially a chronic acid
bleaching agent, has the advantage of
minimizing any tendency to harden the
gelatin in the image portions and, there
dependence of satisfactory balance between the emulsions
in the image portions and, there
fore, facilitates the attainment of satis
fireable 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 simultaneou
sly developed, fixed and bleached out
may be employed in the differential treat
ment of reversed images. In this method
the reversed developable silver salt images
are all developed in the dark to silver and
fixed if necessary whereas 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
ferriyanide 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 the silver
solvent. The two lower layers are then
successively treated in similar manner.

In another method of differential treat
ment, the bleached (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 treat
ment of the layers is to subject the el
ement to differential colour development.
In such differential colour development
the colour developer is permitted to act
upon the image in one layer only at a time.
For the treatment of the film herein
before described the re-exposed reversed
silver salt image in the upper layer only
is colour developed in the dark by con
rolled penetration of a minus blue colour
developer. Such control may be facili
tated 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 appli
cation 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.

\[
\begin{align*}
A & \quad \text{aniline sulphate} \quad 1 \ gm. \\
& \quad \text{Sodium sulphite} \quad 2 \ gm. \\
& \quad \text{Sodium carbonate} \quad 30 \ gm. \\
B & \quad \text{Water} \quad 1 \ litre \\
& \quad \text{4 - nitro - aceto - acet-
& \quad \text{anilide} \quad 2.5 \ gm. \\
& \quad \text{Iso-propyl alcohol} \quad 100 \ cc. \\
\end{align*}
\]

Other known yellow dye forming com
pounds may be used.

The under layers are then successively
colour developed in the dark, first by con
rolled penetration of a magenta (minus
green) colour developer which preferably
contains a loading agent to assist in con
fining its action to an intermediate layer,
and finally by colour developing the bottom
layer to blue green (minus red). Before
each step involving controlled penetra
tion 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 in
creases 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 an
other. Thus the re-exposed reversed
image in the top layer only may be re
developed in the dark to silver and the
images in the remaining layers colour
developed in the dark by the method in
volving 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 exists in one layer only and the images in the other layers have been colour developed, to colour such an image by mordanting and dying 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. 341,163.

Such known reagents may be employed in some of the processes hereinafter described.

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.

Fims 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 of 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 colur 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 10 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 180
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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