[Second Edition.]

PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION.

Improvements in and relating to Colour Photography.

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

This invention relates to 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. The present invention may be employed, for example, in the processing of the sensitive element, especially a film, which is described and claimed in our co-pending application No. 26523/34.

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 sensitised 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, it is first 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 and developed with a minus red colour forming developer. This converts the silver salts in all the layers to 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 methyl 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 hydroxylamide 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 development to the colours complementary to the colours to which the respective layers were sensitised. The process may 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 31st day of May, 1935.
W. P. THOMPSON & CO.,
12, Church Street, Liverpool, 1,
Chartered Patent Agents.

COMPLETE SPECIFICATION.

Improvements in and relating to Colour Photography.

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

This invention relates to colour photographic processes and in particular to the production of 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.

Methods of producing a colour photograph comprising forming in superimposed layers of emulsion sensitized respectively to record different colour values, superimposed latent images of different colour sensations simultaneously developing and then fixing said images, then successively forming colour images in the different layers by bleaching and re-developing with developers containing respectively different colour-formers, are

described in Specification No. 376,838.

In our prior specification No. 427,516 we have described and claimed a method of colour processing a photographic element having a plurality of superimposed layers containing different colour sensation silver salt records on the same side of a single support which includes colour developing all the silver salt records in the layers to one colour, fixing if necessary, and then bleaching the colour developed records in all except the bottom layer to remove and/or destroy the colour and reconvert the silver which was developed therewith into developable silver salt. More specifically we have described and claimed a method of colour processing photographic elements having a plurality of superimposed layers containing different colour sensation silver salt records on the same side of a single support which includes colour developing all the silver salt records in the layers, fixing if necessary and then bleaching the colour developed record in an upper layer to remove and/or destroy the colour and reconvert the silver which was developed therewith into developable silver salt without materially affecting the colour developed record in the layer immediately therebeneath. In the preferred manner of processing a film described in detail in that specification the negative film carried two sensitive emulsions on the same side of the support sensitized to red and green respectively while the positive film carried two sensitive emulsions sensitized to red and green respectively on one side of the support and a sensitive emulsion sensitized to infra-red on the other side of the support.

The object of the present invention is to provide new or improved methods for the production of a photographic record in the minus colours of the original by converting into coloured image records superimposed latent image records of different colour sensations substantially covering the whole of the visible spectrum produced respectively in at least three gelatino-silver halide emulsion layers inseparably coated on the same side of a single support by a single exposure of all the layers from one face whereby such latent images lie accurately superimposed and mostly in the corresponding strata of each layer. A process is described in United States Specification No. 1,966,330 for making two-colour prints on double coated film. In this process a photographic film is employed which is coated on both sides of the support with a light-sensitive emulsion, preferably containing a water-soluble non-actinic dye to prevent printing through. This film is printed on one side from a red filter negative and printed either successively or simultaneously and in register on the other side from a blue-green filter negative. The film is then developed on both sides in a developer which forms a silver image and an associated colour image. After fixing and washing, the film is now treated on one side with a reagent which destroys or eliminates the colour and which converts the silver to a silver salt. The silver salt image is then converted to an image complementary in colour to the colour first formed. It is stated that the process is capable of being carried out with substantially the same procedure in a rather thick heavily dyed single layer in which case the images are formed at or near the opposite surfaces of the same layer. It is further stated that for treatment of one image a concentrated bath would be used for a controlled short interval followed by a stop bath.

The new or improved methods according to the present invention present advantages over any hitherto proposed and known to use. In carrying out the present invention in most of its forms it is not necessary, for instance, to cause a colour developer to come into contact with an already colour developed image. Since all the layers are on the one side of the film such film is particularly useful for taking pictures in small sizes such as 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, the process includes simultaneous colour development of the silver salt images in at least two of the layers and subsequent bleaching of less than all of the colour developed images to decolourise and/or remove the colour and reconvert the silver which was developed therewith into a silver salt image or images. Most suitably the superimposed latent image records consist of records of red, green and blue respectively contained in three gelatino-silver halide emulsion layers preferably having clear gelatine layers therebetween.

According to a further feature of the invention there is provided a process for the production of a photographic record in the minus colours of the original by converting into coloured image records superimposed latent image records of different colour sensations substantially converting the whole of the visible spectrum which have been produced respectively in three gelatino-silver halide

emulsion layers inseparably coated on the same side of a single support (and preferably having clear gelatine layers therebetween) by a single exposure of all the layers from one face whereby such latent images lie accurately superimposed and mostly in the corresponding strata of each layer, which process includes simultaneously developing the silver salt images in all the layers to the minus colour required in the lowest layer, fixing if necessary, bleaching the colour developed images in the upper two layers only to decolourise and/or remove the colour and reconvert the silver which was developed therewith into silver salt images and thereafter processing the bleached images in the upper two layers to the two different minus colours required in those layers. The bleached silver salt images in the upper two layers may be colour developed to the minus colour required in the middle layer, whereafter the upper layer only is bleached and then processed to the minus colour required in that layer, preferably by colour development.

The colour processing of the silver salt images in the upper two layers may, alternatively, include the step of submitting these emulsion layers to a colour developer whose penetration is so controlled as to restrict the development to the uppermost layer whereafter the lower one of the upper two layers is colour developed. This modification, while it reduces the number of processing steps, may not give results which are quite so satisfactory as those which can be obtained by the method just given.

When the images in all the layers have been colour developed, the silver can be removed by known means leaving clear transparent dye images.

According to a still further feature of the invention, preferably after development of the latent images in all the layers to silver images, fixation and bleaching, the silver salt images in the two upper layers only are developed to silver images, the silver salt image in the bottom layer is colour developed to the minus colour required in that layer, the images in all the layers are fixed if necessary, the silver images in the upper two layers are bleached and colour developed to the minus colour required in the middle layer, the upper layer only is bleached to decolourise and/or remove the colour and reconvert the silver which was developed therewith into a silver salt image, the silver salt image in the top layer is colour developed to the minus colour required in that layer and finally the silver is removed from all the layers leaving clear transparent dye images. The first step of this can be accomplished by submitting the photographic elements to an ordinary developer whose penetration is so controlled as to restrict its action to the upper two layers.

In selecting the appropriate shade of the minus colour regard must be had to the nature of the light to be used in subsequent use of the colour-processed element.

Prior to the colour processing it may be desirable to develop in the dark the latent images in all the layers to silver and then fix, wash, rebleach and dry the element. This procedure has the advantage that the element so developed can be fixed, thus avoiding differential fixation of the layers which might otherwise be required in some of those modifications of the colour processing which do not involve, as the first step, simultaneous development of the images in all the layers. Moreover, the silver development is easy to control and need not be carried to completion if it is found that the images would thereby be too dense. On the other hand shorter exposure in the camera is required to produce images of adequate density if an energetic silver developer can be used. Finally, the developed images can be rebleached with ammoniacal ferricyanide to silver ferrocyanide which is readily reducible to silver, even without exposure to light.

For use in three-colour photography, the photographic element which is to be processed by the present invention has three gelatino-silver halide emulsion layers which are respectively sensitized to red, green and blue. The latent images which are produced in these layers on exposure of the element in a camera or otherwise therefore represent the records of these colour components of the exposing light. It is desirable that the sensitization of the layers be such that the record of blue does not lie between those of the red and green. The records are preferably in the order red, green and blue upwards from the support.

It will be apparent that if the latent images are produced by printing from a negative in minus colours, the processing of the photographic element in minus colours will then result in a natural three colour photograph and the process of the present invention may therefore be employed for the production of positives or negatives.

An important feature of the invention is a process for the production of a photographic record in the minus colours of the original by converting into coloured image records superimposed latent image records of the red, green and blue colour

sensations produced respectively in three gelatino-silver halide emulsion layers inseparably coated on the same side of a single support by a single exposure of all the layers from one face whereby such latent images lie accurately superimposed and mostly in the corresponding strata of each layer, which process consists in submitting the emulsion layers to a colour developer which develops all the silver salt images to the colour required in the lowermost emulsion layer, then fixing if necessary, then submitting the emulsion layers to a bleaching agent whose penetration is so controlled as to restrict its action to the two upper emulsion layers the colour developed images in which are thereby decolourized and reconverted to silver salt, then submitting the emulsion layers to a colour developer which develops the decolourized and reconverted silver salt images in both the upper layers to the colour required in the middle layer, then submitting the emulsion layers to a bleaching agent whose penetration is so controlled as to restrict its action to the uppermost layer the colour developed image in which is thereby decolourized and reconverted to silver salt, then submitting the emulsion layers to a colour developer which develops the decolourized and reconverted silver salt image in the uppermost layer to the colour required therein, and finally removing the silver from all the layers to leave 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 for example in patent specification No. 376,838. Such colour formers are organic compounds acting as couplers in connection with certain photographic developers to form coloured compounds usually insoluble in water, together with the finely divided silver which is being formed by the 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 as possible. It must, however, 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 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 naphthocyanol 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 intermediately 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 efficiency of the filtering required. Suitable dyes are, for example, tartrazine (about 0.25 to 0.5 m.gm. per square cm.) which is removable or 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 employed in all the emulsion layers may be silver bromide.

If the film is to be exposed in a camera rapid emulsions should be used. If the film is to be exposed by printing fine grained emulsions giving high definition 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 processing the element after it has been exposed for the production of latent images in the layers.

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 now contains negative latent images in all the layers which have to be processed to the minus colours of the colours to which the layers were sensitized. If the negative element is to be used for printing, the dyes employed should have as sharp an absorption band as possible to afford efficient printing images.

In carrying out the differential processing of the layers, use is made of the methods described and claimed in our co-pending applications Nos. 427,516 and 427,520. The negative latent images in all the layers are first colour developed in the dark to minus red. The developer may contain a para-amino aniline as the developing agent and a hydroxy diphenyl as a coupling or dye-forming component 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 gm.
	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 gelatine 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 any 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.

Instead of developing the latent images in all the layers to minus red, the element may be subjected in the dark to 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 then fixed, washed and the negative silver images bleached to silver salt images with an ammoniacal ferricyanide bath or a hydrobromic acid oxidising bleach bath, for example.

If the above bleaching operation is carried out in the dark with an oxidising hydrohalide bleach bath, the film will contain silver halide images in all the layers which have to be rendered developable before submitting them to the minus red colour developer in the subsequent differential processing. For this purpose they are preferably exposed to white light, the duration of exposure being determined by the density of the images. The silver salt images in all the layers are then colour developed minus red as hereinbefore described, and fixed if necessary.

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 reconversion 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 this 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 acēto 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 innermost 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 therein to metallic silver and forms a yellow (minus blue) dye at the points at which metallic silver is formed. A suitable minus blue dye forming compound is 4 - nitro - acetoacetanilide, although other substituted aceto-acetanilides or other well known yellow dye forming compounds may be used. We make no claim herein to the use of substituted 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 a metallic silver in each of the layers. The metallic silver is removed in a suitable bath such as Farmer's solution, leaving clear transparent dye images in the film. The film is then washed and dried and is negative in minus colours from which a natural colour photograph may be obtained by printing on a similarly constructed film and processing by the same methods.

An alternative method of differential treatment of the latent or developed, fixed and subsequently bleached images in the layers, is to develop 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 as in specification No. 376,838. This control of penetration is facilitated by using a developer solution containing a high concentration of a loading agent, such as sodium sulphate. This development must be done in the dark if any unexposed silver halide is present. 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 32° F. to 40° F. 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 salt 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 in a blue-green (minus red) colour forming developer (in the dark if latent image is to be treated) 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 now, in all cases, be carried out in the light. The silver images in the outer layers are then 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 are then colour developed to minus green, the film washed and dried, and the upper layer only bleached and redeveloped 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 satis-

factory balance between the emulsions throughout the useful density range.

In another method of differential treatment, the latent (or developed, fixed and subsequently bleached) images in all the layers are developed (in the dark if any unexposed silver halide is present) with a blue-green (minus red) colour developer and fixed if necessary. The subsequent operations can then be carried out in the 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 redeveloped 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. Alternatively a colour developer may be permitted to act upon the bleached image in the top layer only. This is effected 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 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 may use the formula already given in which the iso-propyl alcohol acts, in part at least, as a loading agent. Known yellow dye-forming compounds other than those given in the formula may, however, be used.

The bleached under layer is then colour developed with a magenta (minus green) colour developer which preferably contains a loading agent to assist in confining its action to this intermediate layer. Before the step involving controlled penetration of a colour developer the film must be thoroughly dried.

In such operation of selective colour development it may be desirable to add to the developer a substance e.g. a thiocyanate which increases the reduction potential of the developer but we make no claim to this in the present application.

It will be apparent 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.

The film thus obtained consists of a clear transparent support carrying accurately superimposed clear transparent dye images containing substantially no silver so that there is very little loss of light when the film is viewed as a transparency. Moreover, colour fringing is impossible.

While it is preferable to produce coloured images in all the layers 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 a silver image by mordanting and dye toning.

Whenever it is necessary, during the processing, to render bleached 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 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 in general to elements having three or more gelatino-silver halide emulsion layers inseparably coated on the same side of a single support containing different colour sensation records in any order which have been produced by a single exposure of all the layers from one face.

The emulsion layers may be coated on a paper or other support to enable the processed element 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. Process for the production of a photographic record in the minus colours of the original by converting into coloured image records superimposed latent image records of different colour sensations covering substantially the whole of the visible spectrum which have been produced respectively in at least three gelatino-silver halide emulsion layers inseparably coated on the same side of a single support by a single exposure of all the layers from one face whereby such latent images lie accurately superimposed and mostly in the corresponding strata of each layer, which process includes simultaneous colour

development of the silver salt images in at least two of the layers and subsequent bleaching of less than all of the colour developed images to decolourise and/or remove the colour and reconvert the silver which was developed therewith into a silver salt image or images.

2. Process as claimed in claim 1 in which the superimposed latent image records consist of records of red, green and blue, respectively contained in three gelatino-silver halide emulsion layers preferably having clear gelatine layers therebetween.

3. Process for the production of a photographic record in the minus colours of the original by converting into coloured image records superimposed latent image records of different colour sensations covering substantially the whole of the visible spectrum which have been produced respectively in three gelatino-silver halide emulsion layers inseparably coated on the same side of a single support (and preferably having clear gelatine layers therebetween) by a single exposure of all the layers from one face whereby such latent images lie accurately superimposed and mostly in the corresponding strata of each layer, which process includes simultaneously colour developing the silver salt images in all the layers to the minus colour required in the lowest layer, fixing if necessary bleaching the colour developed images in the upper two layers only to decolourise and/or remove the colour and reconvert the silver which was developed therewith into silver salt images and thereafter processing the bleached images in the upper two layers to the two different minus colours required in those layers.

4. Process as claimed in claim 3 in which the three gelatino-silver halide emulsion layers, respectively contain latent image records of red, green and blue and the latent image record of the blue does not lie between those of the red and green.

5. Process as claimed in Claim 2 or 4 in which the latent image records are in the order red, green and blue upwards from the support.

6. Process as claimed in either of claims 3 or 4, in which the bleached silver salt images in the upper two layers are colour developed to the minus colour required in the middle layer whereafter the upper layer only is bleached to decolourise and/or remove the colour and reconvert the silver which was developed therewith into a silver salt image and thereafter the bleached silver salt image in the upper layer is processed to the minus colour required in that layer.

7. Process for the production of a photographic record in the minus colours of the original by converting into coloured image records superimposed latent image records of the red, green and blue colour sensations produced respectively in three gelatino-silver halide emulsion layers inseparably coated on the same side of a single support by a single exposure of all the layers from one face whereby such latent images lie accurately superimposed and mostly in the corresponding strata of each layer, which process consists in submitting the emulsion layers to a colour developer which develops all the silver salt images to the colour required in the lowermost emulsion layer, then fixing if necessary, then submitting the emulsion layers to a bleaching agent whose penetration is so controlled as to restrict its action to the two upper emulsion layers the colour developed images in which are thereby decolourized and reconverted to silver salt, then submitting the emulsion layers to a colour developer which develops the decolourized and reconverted silver salt images in both the upper layers to the colour required in the middle layer, then submitting the emulsion layers to a bleaching agent whose penetration is so controlled as to restrict its action to the uppermost layer the colour developed image in which is thereby decolourized and reconverted to the silver salt, then submitting the emulsion layers to a colour developer which develops the decolourized and reconverted silver salt image in the uppermost layer to the colour required therein and finally removing the silver from all the layers to leave clear transparent dye images.

8. Process as claimed in any of the preceding claims in which the latent image records are first simultaneously developed to silver, fixed, bleached to silver salt images and thereafter colour developed.

9. Process as claimed in either of Claims 3 or 4, in which the bleached silver salt image in the upper layer only is redeveloped to silver, the bleached silver salt image in the middle layer is colour developed to the minus colour required in this layer, and the re-developed silver image in the upper layer only is processed to the minus colour required in that layer.

10. Process as claimed in Claim 9 in which the redeveloped silver image in the upper layer only is bleached to a silver salt image and thereafter colour developed to the minus colour required in that layer and finally the silver is removed from all the layers leaving clear transparent dye images.

11. Process as claimed in Claim 2 in which, preferably after development of

the latent images in all the layers to silver images, fixation and bleaching, the silver salt images in the upper two layers only are developed to silver images, the silver salt image in the bottom layer is colour developed to the minus colour required in that layer, the images in all the layers are fixed if necessary, the silver images in the upper two layers are bleached and colour developed to the minus colour required in the middle layer, the upper layer only is bleached to decolourise and/or remove the colour and re-convert the silver which was developed therewith into a silver salt image, the silver salt image in the top layer is colour developed to the minus colour required in that layer and finally the silver is removed from all the layers leaving clear transparent dye images.

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