

PATENT SPECIFICATION

Application Date: June 1, 1935. No. 9734/36.

455,128

(Divided out of No. 447,092).

Complete Specification Accepted: Oct. 14, 1936.



COMPLETE SPECIFICATION

Improvements in and relating to Colour Photography

We, KODAK LIMITED, a Company registered under the Laws of Great Britain, 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 Company organised under the Laws of the State of New York, United States of America, of 343, State Street, Rochester, 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 constructed positive photographic element which, after processing, gives a representation in substantially true colours.

In Specification No. 376,838 there is described and claimed a method of producing a colour photograph which comprises 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. It is stated that the numbers of layers of differently sensitized layers to be treated is not limited to two or three, though three layers is generally the maximum number desired. A way of carrying out that invention is to separate the treatment of the developed, fixed and washed film or plate for subsequent colouring by method of controlled diffusion of chemical solutions. The coatings may be simultaneously bleached in potassium ferricyanide and the upper one (or two in the case of a triple coating) alone re-developed by controlled diffusion of a concentrated developer. The undeveloped lower layer, still containing an image-record in silver ferrocyanide, may be developed by immersion in a colour-forming developer as described above which will not affect the re-developed silver of the upper layer or layers. The plate or film, may be fixed in sodium thiosulphate, washed and then dried, and the remaining layer or layers bleached to silver ferrocyanide for redevelopment in another colour forming developer, and so on to the third coating in the case of three colour photography.

In Specification No. 427,518 we have described and claimed improvements in or modifications of that type of process, i.e. in which the action of a bleaching bath or a developing bath, as the case may be, is to be restricted to an upper layer leaving a lower layer not materially affected thereby. In carrying out such a process the action of the processing bath has to be arrested before it has substantially penetrated a lower layer and materially affected the image therein.

In our co-pending application No. 447,092 we have described 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

[Price 1/-]

Also 245

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.

All of such methods described in application No. 447,092 included 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 consisted of records of red, green and blue respectively contained in three gelatino-silver halide emulsion layers preferably having clear gelatine layers therebetween.

The present invention is concerned with alternative methods for the production of a photographic record as described above which, while they may not give results which are quite so satisfactory as those which can be obtained by the methods described in application No. 447,092, involve fewer processing steps and fewer reagents and may therefore, in certain cases, be more economical in time and materials.

According to the present invention the process includes submitting the emulsion layers without reversal of the images therein to a colour developer whose penetration is so controlled as to restrict the development to an upper layer or upper layers. This involves arresting the action of the processing bath before it has substantially penetrated and materially affected the image in the layer immediately below that in which development is being effected. Preferably control of the diffusion of the colour developer is facilitated by the presence therein of a water-soluble loading agent as claimed in co-pending application No. 25940/36, (Serial No. 454,622). The silver salt images may therefore be processed to colour by submitting the emulsion layers to a succession of different colour developers, the penetration of each of which is so controlled as to restrict its developing action to the uppermost undeveloped layer, whereby the layers are successively affected by the colour developers commencing with the uppermost and finishing with the lowermost layer on the support.

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, bleach the silver images to silver salt images 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. 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 re-bleached 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.

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 colloiddally dispersed in a gelatine layer even when the silver has been removed. It is thus possible to produce by this means a substantially coloured image in proportion to the extent and depth of the original silver image. The expression "Colour develop-

70

75

80

85

90

95

100

105

110

115

120

125

130

ment" when used herein does not therefore include the known process in which colour formers are incorporated in the layers themselves.

5 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 green 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.

30 Such a film may be that described in greater detail in application No. 447,092. 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.

40 The film is then 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.

50 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.

55 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.

60 In the preferred method of processing, the film is subjected in the dark to an

ordinary developer forming silver images in all the layers.

A suitable developer has the formula:—

Monomethyl- <i>p</i> -aminophenol		
sulphate	5 gm.	70
Hydroquinone	10 gm.	
Sodium Sulphite	75 gm.	
Sodium Carbonate	30 gm.	
Potassium Thiocyanate	1.75 gm.	
Potassium Bromide	2.5 gm.	75
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 80 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 85 layers which have to be rendered developable before submitting them to the colour developers in the subsequent differential processing. For this purpose they are preferably exposed to white light, the dura- 90 tion of exposure being determined by the density of the images.

The film is now subjected to differential colour development. For this purpose the silver salt image in the upper layer only 95 is colour developed by controlled penetration of a colour developer. Such control may be facilitated by the presence in the colour developer of a loading agent as described and claimed in co-pending applica- 100 tion No. 25940/36, (Serial No. 454,622). An example of the minus blue colour developer first employed to which loading agents may be added, is the following:— Known yellow dye forming compounds 105 other than those given in the formula may however, be used.

(a) <i>p</i> -amino dimethyl aniline		
sulphate	1 gm.	
Sodium sulphite	2 gm.	110
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))		115

The film now contains a minus blue (yellow) image in the upper layer only and silver salt images in the lower two layers. It is next submitted to controlled penetra- 120 tion of a magenta (minus green) colour developer which preferably also contains a loading agent to assist in confining its action to the middle layer.

Such a developer may contain as the colour-forming component *p*-nitrophenyl 125 aceto nitrile, which couples with the

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

The minus green developer may have the following composition :

5	(a)	2-amino 5-diethyl amino toluene hydrochloride	1 gm.
		Sodium sulphite	10 gm.
		Sodium carbonate	30 gm.
		Potassium thiocyanate	0.5 gm.
10		Water to	1000 cc.

	(b)	<i>p</i> -nitrophenyl aceto nitrile	0.75 gm.
		Acetone	20 cc.
		Iso-propyl alcohol	100 cc.
15		(In use, (b) is added to (a)).	

In this formula also the iso-propyl acts, in part at least, as a loading agent.

The film now contains a minus blue (yellow) image in the upper layer only, a minus green (magenta) image in the middle layer only, and a silver salt image in the lower layer. It is next submitted to a minus red colour developer.

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)	<i>p</i> -amino diethyl aniline monohydrochloride	3 gm.
35		Sodium sulphite	5 gm.
		Sodium carbonate	50 gm.
		Potassium thiocyanate	0.5 gm.
		Water to	1000 cc.

	(b)	<i>m</i> -hydroxy diphenyl	2.5 gm.
40		Methyl alcohol	100 cc.
		(For use, add solution (b) to solution (a).)	

The potassium thiocyanate used in this and the preceding developing formula is not essential but serves to increase the reduction potential of the developer as set forth in our co-pending application No. 8920/35, (453,233).

Before each step involving controlled penetration of a colour developer the film must be thoroughly dried.

The metallic silver is finally removed from the film by a suitable bath such as Farmer's solution leaving clear transparent dye images. The film is then washed and dried and is a 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.

60 These operations of selective colour

development must be carried out in the dark if the film contains any unexposed silver halide and in this event are preferably each followed by fixing of the colour developed image. Such fixing may be accomplished by controlled penetration of a fixing agent following each controlled penetration of a colour developer. Such controlled penetration may be facilitated by the presence in the fixing bath of a loading agent as described and claimed in our co-pending application No. 25940/36, (Serial No. 454,622).

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.

An alternative method of treatment is to redevelop the silver salt image in the top layer only to silver and then colour develop the images in the remaining layers by the method involving controlled penetration of a colour developer as just described. If the element contains any unexposed silver halide these operations must be performed in the dark whereafter the element is fixed. Subsequent operations can now be performed in the light. Thereafter the silver image in the top layer only may be bleached and the bleached image redeveloped with a colour developer.

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 submitting the emulsion layers without reversal of the images therein to a colour developer whose penetration is so controlled as to restrict the development to an upper layer or upper layers.

2. A process as claimed in claim 1 in which the silver salt images are processed to colour by submitting the emulsion layers to a succession of different colour developers, the penetration of each of which is so controlled as to restrict its developing action to the uppermost undeveloped layer.

3. A process as claimed in claim 1 or 2 in which the photographic element has three gelatino-silver halide emulsion layers inseparably coated on the same side of a

single support (preferably with clear gelatine layers therebetween) containing respectively 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.

4. A process as claimed in claim 3 in which the latent image records are in the order red, green and blue upwards from the support.

5. Process as claimed in any of the preceding claims in which the silver salt images to be colour developed are produced by first simultaneously developing the latent images to silver, then fixing and bleaching.

6. Process for the production of a multi-layer photographic record in minus colours by differential colour development without reversal of the images in the layers, substantially as herein described.

Dated this 1st day of April, 1936.

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