

PATENT SPECIFICATION

427,518

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COMPLETE SPECIFICATION.

Improvements in Colour Photography.

We, KODAK LIMITED, a British Company, of Kodak House, Kingsway, London, W.C.2, Assignees of LEOPOLD DAMROSCH MANNES and LEOPOLD GODOWSKY, Junior, both Citizens of the United States of America, both of Kodak Park, Rochester, New York, United States of America, do hereby declare the nature of this invention 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 photographic processes and particularly those adapted to colour motion pictures.

The invention relates to the processing of photographic elements having a plurality of superimposed layers containing different colour sensation records on the same side of a single support, and in particular the invention relates to the type of processing 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 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.

A method of this type is utilised in carrying out the invention described and claimed in the specification of Patent No. 376,838. According to that specification the method of producing a colour photograph 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 number 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 methods 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 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 re-development in another colour forming developer, and so on to the third coating in the case of three colour photography.

The present invention relates to various improvements in or modifications of a process of the type hereinbefore defined, which are designed to facilitate the controlled diffusion or restriction of action of the bleaching bath or developing bath as the case may be and thus improve the result and enable colour photographs of excellent quality to be produced in a commercially convenient manner.

According to one feature of the present invention, in a process of the type defined, control of the diffusion of the bleaching bath or the developing bath, as the case may be, is facilitated by the presence therein of a water-soluble loading agent. By this means the rate of penetration of the processing bath is reduced and it then becomes more readily possible to arrest its action before it has substantially penetrated a lower layer and materially affected the image therein.

According to another feature of the invention, in a process of the type defined, control of the diffusion of the bleaching bath or the developing bath, as the case may be, is facilitated by the presence between the emulsion layer on which the bath is to act and the emulsion layer therebeneath of a thin layer of clear gelatine, and, if desired, by the presence in the bath of a water-soluble loading agent.

This affords leeway in arresting the action of the processing bath before it has substantially penetrated a lower layer and materially affected the image therein.

According to another feature of the present invention, in a process of the type defined, the action of the developing bath, containing a water-soluble loading agent or not, is arrested by suddenly submitting the photographic element to a low temperature preferably by subjecting it to the action of an acid stop bath at a low temperature. According to yet another feature of the present invention, in a process of the type defined the diffusion of a ferricyanide bleaching bath, containing a water-soluble loading agent or not, is arrested by suddenly submitting the photographic element to the action of a stop bath containing hydroxylamine or hydrazine.

The use of loading agents in photographic developers is known. Thus developers for use in tropical countries have been suggested in which quantities up to about 20% of a salt such as crystalline sodium sulphate or potassium sulphate or ammonium sulphate are included for the purpose of retarding the swelling of the gelatine. Chrome Alum has also been added to amidol developers for the same purpose. The development is also slowed down by the presence of such salts but for the purposes to which such developers were put, this was a disadvantage because at high temperatures it is important to work quickly to avoid trouble due to the softening of the gelatine. Other developers have also been proposed for use in tropical countries such as metol-hydroquinone developer containing besides the usual ingredients, 8% of acetone and 1.5% of formalin. Also the use of 50% alcohol has been suggested for the same purpose. The use of sugar for this purpose has been suggested. It is also known to add to developing solutions such substances as glycerine and treacle which by increasing the viscosity confines the development to the surface of ordinary black and white photographic prints the purpose being usually to produce "soft" or other "artistic" effects.

So far as the process of the present invention is directed to improvements in the control of differential development of multi-layers in colour photography, it is not to be confused with processes in which the layers are all developed as near as possible to the same extent since these latter processes do not involve the step of arresting the action of the developer before it has penetrated a lower layer and materially

affected the image therein. So far as we are aware it has not hitherto been known to load photographic developing or bleaching baths, with loading agents for the purpose of assisting in confining the action of the reagent to an upper of a plurality of layers on a single support.

In carrying out the present invention suitable water-soluble loading agents are sodium sulphate or water-soluble organic liquids such as methanol.

The use of intermediate layers of clear gelatine between the emulsion layers of a multi-layer photographic element is broadly known. Such intermediate layers have been suggested for the purpose of preventing wandering of the sensitizing dyes or similar bodies in the emulsions from one emulsion layer to another, or for subsequent hardening to produce a hardened layer impermeable to dyestuff.

The improvements according to the present invention may be applied to the processing of negative or positive photographic elements.

The invention will be illustrated, by way of example, with reference to the processes described in co-pending applications Nos. 26084/33, (Serial No. 427,472), 18932/34 (Serial No. 427,516) and 18936/34 (Serial No. 427,520).

The film therein described consists of a support carrying superposed layers of green-sensitized and red-sensitized emulsions respectively, the green-sensitized emulsion being nearest the support. A thin intermediate layer of unsensitized gelatine is provided between these differentially sensitized layers. Such a negative film may be exposed in a split-beam two-colour camera of the type shown and described in our co-pending application No. 26084/33 (Serial No. 427,472). The exposed film is then processed to produce an image in the lower layer colour developed to a minus green colour and an image in the upper layer colour developed to a minus red colour.

The unsensitized clear gelatine intermediate layer affords protection against possible wandering of the sensitizing dyes from one emulsion to the other and also gives latitude in the differential treatment of the layers described herein after.

In processing the exposed film by the method described in co-pending applications Nos. 18932/34 (Serial No. 427,516) or 18936/34 (Serial No. 427,520) both layers are first colour developed to minus green and then the upper one only is bleached before colour developing to minus red. This bleaching step is the critical one in the colour differentiation

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between the two layers and depends on restricting the penetration of a bleaching solution to the depth of one layer only. An ordinary dilute water solution would penetrate the surface layer in 1 to 2 seconds. By using a high concentration of a loading agent such as alcohol, the time may be greatly extended. A 75% methanol and 5% water solution containing chromic acid, hydrobromic acid and potassium bromide bleaches the surface layer in 15 to 30 seconds, depending upon temperature and the thickness of the emulsion coating.

The following is a satisfactory formula for this bleach:

FORMULA I.

Chromic acid, 10% solution	-	10	cc.
Hydro-bromic acid 41% solution	-	3	cc.
Potassium bromide	-	2	gram.
Methanol	-	300	cc.
Water	-	90	cc.

The time of immersion in this bleach is carefully measured by trial, which is easily done, and after the bleaching bath the film is immediately immersed in a stop bath of this formula:

FORMULA II.

Ammonia 28%	-	5	cc.
Water	-	100	cc.

The action of this bleach bath is to convert to silver bromide the silver in the top emulsion layer only and to bleach the dye formed with the silver image to a colourless compound which is very soluble in the alcohol of the bleach bath. The bleaching action would continue undesirably to the lower layer if not checked. Also, some of the undissolved bleached dye would be restored to colour in the image again as the acid was gradually washed out of the film. To check the bleaching action quickly and prevent restoration of dye, the stop bath given is used with very satisfactory effect. An alternative formula for a stop bath is the following.

FORMULA III.

Methanol	-	400	cc.
Sodium sulphite	-	20	gram.
Ammonia 28%	-	10	cc.
Water to make 1 litre.			

The sodium sulphite inhibits restoration of the dye, while the methanol dissolves out the bleached dye compound.

The step involving bleach and stop bath is most practicable in a processing machine where time and temperature control may be maintained within reasonable limits of variation. To allow for some error, the thin gelatine layer between the two emulsions has been found to afford sufficient tolerance. That layer may be about one-half the thickness of the emul-

sion coatings.

In our co-pending application No. 26084/33 (Serial No. 427,472) we have described an alternative method of processing in which the exposed and bleached film is again exposed and the top layer only is redeveloped to silver. In such a method it is necessary to control the penetration of an energetic developer and arrest the development as soon as the desired depth is reached. To make the penetration of the developer sufficiently slow to permit adequate control, the developer solution is "loaded" by adding a large amount of sodium sulphate. The following formula represents a satisfactory example.

FORMULA IV.

Hydro-quinone	-	12.5	gram.
Sodium sulphite	-	19.0	gram.
Potassium hydroxide	-	41.0	gram.
Sodium sulphate	-	200	gram.
Water to 1 litre.			

The time of penetration of this developer through the top layer only may be extended to 30—40 seconds, depending on temperature and emulsion thickness. The time of penetration will, of course, depend on the particular developer formula used. Development is arrested by immediate immersion in a stop bath kept at a very low temperature, say, between 0° C.—5° C. Such a stop bath is:

FORMULA V.

Sodium bisulphite	-	50	gram.
Glacial Acetic Acid	-	30	cc.
Water to 1 litre.			

In this control of development use is made of the long induction period of hydro-quinone, together with its sensitivity to temperature which is very marked. Satisfactory differentiation of treatment may be repeatedly obtained by this method.

The caustic hydro-quinone developer just mentioned has one disadvantage—it tends to harden the gelatine where the image develops. To avoid this, a concentrated amidol-sodium sulphite formula may be employed instead. A satisfactory formula is:—

FORMULA VI.

Sodium sulphite	-	100	gram.
Amidol	-	50	gram.
Sodium sulphate	-	200	gram.
Water to 1 litre.			

With this developer, a stop bath of 50 cc. of glacial acetic acid in one litre of water, cooled to 0—5° C. is satisfactory, although the stop bath, Formula V, just given, will also be satisfactory.

After the next stage of the processing, when the lower layer contains minus green dye plus silver and the upper layer contains silver only, it is necessary to

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- bleach the silver image in the upper layer only by controlled diffusion of a potassium ferricyanide bath, which converts the silver image to silver ferrocyanide.
- 5 This bleach bath is also loaded with sodium sulphate to extend the time of penetration through one layer alone to 20—30 seconds, depending on temperature and emulsion thickness. A suitable
- 10 bleach is:
- FORMULA VII.
- | | | |
|----------------------------|-----|-------|
| Sodium sulphate - - | 200 | gram. |
| Potassium ferricyanide - - | 50 | gram. |
| Water to 1 litre. | | |
- 15 Here again the clear gelatine intermediate layer between the two emulsions affords leeway for possible error and excessive wandering of solutions. The bleaching action is arrested by immediate
- 20 immersion of the film in a dilute solution of hydroxyl-amine hydrochloride and ammonia which rapidly converts the remaining potassium ferricyanide
- 25 carried along in the gelatine to potassium ferrocyanide, the latter compound having no bleaching action. Such a suitable stop bath is:—
- FORMULA VIII.
- | | | |
|------------------------------|----|-------|
| Hydroxyl-amine hydrochloride | 20 | gram. |
| Ammonia 28% - - - - | 55 | cc. |
| Water to 1 litre. | | |
- 30 This stop bath is used at room temperature.
- Hydrazine or hydrazine sulphate may
- 35 be substituted for hydroxyl-amine hydrochloride in the above formula.
- Further details of the processing will be found in our co-pending applications already mentioned by number.
- 40 The invention is not limited to the preferred form described above. The two layers of negative material may be coated in the reverse order. The intervening thin gelatine layer between the
- 45 two layers of negative material may contain a dye to act as a screen for the layer underneath.
- While we have described this process and designed it particularly for a colour
- 50 motion picture, we do not wish to be limited to the motion picture field. Similar methods could be applied to the making of still pictures on either plates or
- 55 films.
- It will be noted that both sodium sulphate and alcohol, which are given by way of example as loading agents, have a strong affinity for water.
- 60 In our co-pending applications Nos. 18932/34 (Serial No. 427,516) and 18936/34 (Serial No. 427,520) we have described and claimed particular methods of colour processing a photographic element having continuous layers contain-
- 65 ing different colour sensation records on a single support which include the provision of a clear gelatine layer to facilitate control of the diffusion of a bleaching agent. We make no claim herein to the use of a clear gelatine layer when used in the methods claimed in those applica-
- 70 tions.
- Further in our co-pending application No. 18936/34 (Serial No. 427,520) we have claimed particular methods of colour
- 75 processing a photographic element having contiguous layers containing different colour sensation records on a single support which involves the use of water-soluble loading agents to retard the
- 80 diffusion of a bleaching agent. We make no claim to the use of loading agents in the methods claimed in application No. 18936/34 (Serial No. 427,520).
- Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we
- 85 claim, subject to the foregoing disclaimers, is:—
- 90 1. A colour photographic process of the type defined in which control of the diffusion of the bleaching bath or the developing bath, as the case may be, is facilitated by the presence therein of a
- 95 water-soluble loading agent.
2. A colour photographic process of the type defined in which control of the diffusion of the bleaching bath or the developing bath, as the case may be, is
- 100 facilitated by the presence between the emulsion layer on which the bath is to act and the emulsion layer therebeneath of a thin layer of clear gelatine and, if desired, by the presence in the bath of a
- 105 water-soluble loading agent.
3. A colour photographic process of the type defined in which the action of the developing bath, containing a water-soluble loading agent or not, is arrested
- 110 by suddenly submitting the photographic element to a low temperature.
4. A colour photographic process as claimed in claim 3 in which the action of the developing bath is arrested by suddenly
- 115 subjecting it to the action of an acid stop bath at a low temperature.
5. A colour photographic process of the type defined in which the action of a ferricyanide bleaching bath, containing
- 120 a water-soluble loading agent or not, is arrested by suddenly submitting the photographic element to the action of a stop bath containing hydroxylamine or
- 125 hydrazine.
6. A colour photographic process as claimed in any of the preceding claims, in which the processing bath is loaded with a large quantity of sodium sulphate.
7. A colour photographic process as
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claimed in any of claims 1—5, in which liquid is methanol.

the processing bath is loaded with a large quantity of water-soluble organic liquid.

Dated this 26th day of June, 1934.

5 8. A colour photographic process as claimed in claim 7, in which the organic

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