

PATENT SPECIFICATION



Convention Date (United States): Sept. 21, 1932.

427,517

Application Date (in United Kingdom): Sept. 21, 1933. No. 18933/34.

(Divided out of No. 427,472.)

Complete Specification Accepted: April 23, 1935.

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 colour photographic processes and particularly those adapted to colour motion pictures. More specifically it relates to new or improved processes for the production of multicolour photographs from multilayer films and to films suitable for the production of multicolour photographs by these processes.

According to one feature of the present invention a process for the production of a multicolour photograph from a multilayer film having a layer containing a record of one colour component in silver bromide and another layer composed of silver chloride emulsion containing a record of another colour component includes the steps of developing the record in the silver chloride layer and fixing it without affecting the record in silver bromide. A film suitable for this purpose consists of a single support carrying a plurality of superimposed gelatino-silver halide layers sensitized to different colours of which one, at least, consists of an emulsion of silver chloride.

According to a further feature of the invention a process for the production of a multicolour photograph from a multilayer film having a layer on one side of the support containing a record of one colour component in silver bromide and a layer of silver chloride emulsion on the other side of the support containing a record of another colour component, includes the steps of developing the record in the silver chloride layer and treating the film with ammonia to fix the silver chloride layer without affecting the record in silver bromide. A film suitable for this purpose

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consists of a single support carrying superimposed gelatino-silver halide layers on its opposite sides, of which at least one consists of an emulsion of silver chloride. 55

According to a further feature of the invention a process for the production of a multicolour photograph from an exposed multilayer film having one emulsion layer of silver chloride includes the step of converting the colour sensation record in another gelatino-silver halide emulsion layer to silver bromide without further exposure so as to permit development and fixing of the silver chloride layer without affecting the silver bromide layer which is to be processed to a different colour. 60 65

The invention includes more specifically a film for three colour photography having two layers of silver bromide emulsion sensitized to different colours and a layer of silver chloride emulsion sensitized to a third different colour all superimposed on a single support. 70 75

As will be seen from the description which follows the film preferably has a single emulsion layer on one side of the support consisting of silver chloride emulsion and this single emulsion layer may be protected by a removable waterproof coating thereover. 80

The colour processing employed herein is preferably colour development. This expression is intended to designate a process effected by developing a silver salt image with a developer containing a colour former, as described in Patent Specification No. 376,838. Such colour formers are organic compounds acting as couplers in connection with certain developers to form coloured compounds, usually insoluble in water, in the presence of the finely divided silver which is being formed by reaction. The coloured compound formed may belong, for example, to the class of indophenols, indoanilines and indamines and remains colloiddally 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 85 90 95 100

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original silver image. The expression "colour development" when used herein does not therefore include the known process in which colour formers are
5 incorporated in the layers themselves.

The invention will be illustrated by the following description which is given by way of example.

In the drawings:—

10 Figure 1 is a cross-section of a positive film, constructed according to the present invention, before processing, and

Figure 2 is a cross-section of this positive film after colour processing.

15 In the preferred form of the invention now to be described, this positive film comprises a support 20 having on one side superposed layers 21 and 22 of highly transparent emulsion, the lower 21 being
20 sensitized to green and the upper 22 to red light and separated by a thin gelatine layer 23 and on the other surface carrying a layer 24 sensitive to infra-red light. Such a film containing a layer sensitized
25 to infra-red light, and methods of processing it, are claimed in our co-pending application No. 18935/34 (Serial No. 427,519).

This positive film may be printed upon
30 from a two-layer negative film containing records of three-colour sensations in the manner described fully in our co-pending application No. 26084/33 (Serial No. 427,472).

35 The result of the printing as there described is to print the minus red coloured image of the negative film, representing the red record component, in the red-sensitized top coating 22 of the positive
40 film, the minus green coloured image of the negative film, representing the green record component, on the green sensitive positive lower layer 21, and the blue record component (which is in the form of
45 a minus red coloured image on another part of the negative film) on the reverse side of the positive either by projection through the other two layers or by optical means as stated in the aforementioned co-
50 pending application No. 26084/33 (Serial No. 427,472). The printing of the red and green record components is accomplished with yellow light and the printing
55 of the blue record component with infra-red light. In the resulting positive the record of the red, i.e. of the original component, is in the top layer and is to be processed to a minus red colour. The record of the original green component is
60 in the second layer next the support and is to be processed to minus green, and the record of the blue component has been printed by infra-red light on the reverse side, and is to be processed to a minus
65 blue, i.e. yellow.

The three-layer positive as now printed is then processed to three colours in colour developers with a suitable technique to give the results indicated. This gives the
70 three-colour positive shown in Fig. 2.

In practice the following material has been found to give the best results.

The film base 20 is first coated with a layer 21 of a thickness of the order of .0002 inches of a very rapid emulsion
75 sensitized to the green region of the spectrum between 510-590 m μ , with a maximum at about 550 m μ . A fast emulsion sensitized with erythrosin has been found satisfactory. Over this
80 emulsion is coated a very thin layer say between .0001 and .0003 inches, of clear gelatine 23, clear enough to permit adequate exposure of the green sensitized layer. The final top coating 22 is of the
85 same order of thickness as layer 21 and is a red-sensitized rapid emulsion which has been diluted with an equal weight of gelatine before coating to give greater transparency, less density, less tendency to
90 exhaust the developer diffusing through it, and finally, less tendency to harden the gelatine where the image develops. For this top emulsion layer a fast emulsion has been used, sensitized with a red
95 sensitizer conferring sensitivity primarily in the region between 600 and 700 m μ with a maximum near 650 m μ . Such a sensitizer is naphthocyanol. Both layers are, of course, sensitive to blue. The red
100 sensitive emulsion is placed above the green sensitive emulsion so that when carrying out the subsequent processing, it is the red dye, if any, which is subjected to the restricted bleaching step, herein-
105 after mentioned.

It is important for this red-sensitized layer to use an emulsion that is relatively insensitive to light of wave-lengths between 510 and 590 m μ . For the lower
110 green-sensitized emulsion a corresponding restriction is not necessary, as will be seen. The total thickness of the coatings of this material altogether should not substantially exceed the thickness of a single
115 normal coating on motion picture film as ordinarily supplied.

It is naturally important that these two emulsions, as finally coated, have very similar essential characteristics of
120 latitude, speed, contrast, and maximum density.

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

These positive emulsions are chosen for 130

exceedingly fine grain, fine enough to render the appearance of the double-coated film only faintly opaque. Both of these emulsions are predominantly of silver bromide.

On the reverse side of the film support is a thin coating 24 of slow emulsion, not necessarily transparent, sensitized to the infra-red region from about 750 to 850 mμ.

Over this coating is placed a water-proof stripping varnish layer 25 which may contain dye or lamp-black to serve also as backing necessary to avoid halation, due to reflection of red, green, and infra-red rays from the rear emulsion-air interface.

Benzyl cellulose has been found adaptable to this purpose, as it may be easily stripped from the emulsion surface when it is desired to process the infra-red-sensitized coating as given below. A suitable varnish for this purpose is:

FORMULA I.

- Benzyl cellulose - - - - 150 grm.
- Benzene - - - - - 1550 cc.
- 25 Toluene - - - - - 100 cc.
- Xylene - - - - - 400 cc.

(The manufacture of a low viscosity benzyl cellulose suitable for this purpose is described in British Patent Specifications Nos. 327,714, 329,902 and 356,308).

This infra-red-sensitive emulsion is in the form of a pure silver chloride emulsion of whatever grain size may be necessary to secure sufficient latitude. An infra-red sensitizer which is suitable for this emulsion is neocyanine (thio-tricarbo-cyanine).

The infra-red sensitizing of such a chloride emulsion has been found to confer sufficient speed to infra-red light for practical purposes.

The reason for having this single emulsion coating composed of pure silver chloride is to permit of differential fixation in ammonia which will dissolve the silver chloride of this single layer without appreciably affecting the silver bromide formed in a subsequent bleaching step of the positive processing which will be described later.

COLOUR PROCESSING THE PRINTED FILM.

The printed material has a water-proof varnish layer 25 on one side so that the double layer side only is treated at this point. The first steps of the processing are development of the images in a red (minus green) colour developer, and treatment of the film in a bleach which is restricted to the depth of one layer only.

Such processing may be carried out by the methods described and claimed in our co-pending Applications Nos. 18932/24 (Serial No. 427,516), and 18936/34 (Serial No. 427,520).

For the red (minus green) colour

developer we prefer the following solution for the positive red images:

FORMULA II.

- Water - - - - - 1 litre
- Diethyl para - phenylene diamina HCl - - - - 10 grm.
- Sodium sulphite - - - - 5 grm.
- Sodium carbonate - - - 20 grm.
- Potassium bromide (Molar Solution) - - - - - 2 cc.

To 100 cc. of this solution add brom-thio-indoxyl 0.05 grm.

The above differential treatment leaves the film with silver plus dye in the lower layer, and silver bromide in the upper layer. Therefore, subsequent exposure and immersion in a colour-forming developer will cause development only in the top layer where the image is formed of silver bromide.

At the stage where the top layer only of the double coating has been bleached to silver bromide and the dye in that layer removed coincidentally, the protective varnish 25 is removed from the infra-red-sensitive layer 24 at the back of the film. This varnish layer is easily stripped when dry. The film is now immersed in a pure yellow (minus blue) colour-forming developer.

A suitable formula for the yellow colour developer is:—

FORMULA III.

- Water - - - - - 1 litre
- Diethyl - p - phenylene diamine HCl - - - - 10 grm.
- Sodium sulphite - - - - 5 grm.
- Sodium carbonate - - - 20 grm.
- Potassium bromide (Molar Solution) - - - - - 2 cc.

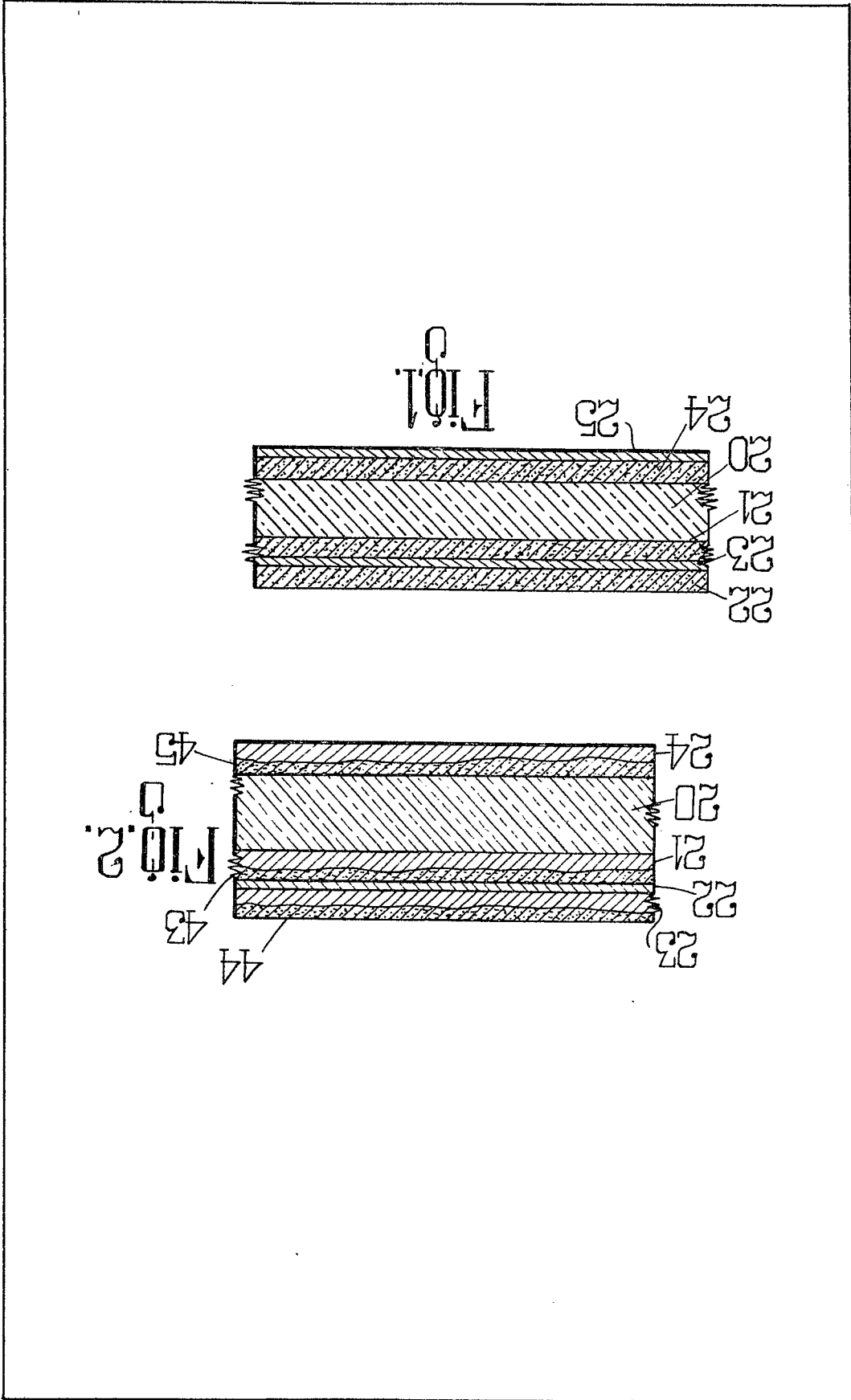
To 100 cc. of this solution are added benzoyl acetone 0.1 grm. dissolved in ethyl alcohol 5 cc.

Other yellow couplers are possible and available. Besides benzoyl acetones, aceto-acetic esters have been employed as couplers with diethyl-para-phenylenediamine as developer.

After the yellow development, the film is immersed in dilute ammonia, approximately 4%, to fix out the undeveloped silver chloride in the infra-red-sensitive layer without affecting the silver bromide formed by the bleach bath in the top layer of the double coating. This silver bromide is therefore the only developable deposit in the film and is developed after exposure to white light in a minus red colour-forming developer in the manner set forth in our co-pending application No. 26084/33.

After thorough washing, the residual images remaining in all three emulsions are simultaneously removed by a simple reduction with Farmer's reducer.

- The film is now washed and dried and is a complete three colour subtractive picture, as shown in Figure 2 in which there are shown in the three original layers 23, 21 and 24 respectively, the dye images 44, 43 and 45 which successively absorb red, green and blue, and by the subtractive process transmit a properly coloured three colour image.
- 10 The order of the emulsion layers of the positive with respect to the direction of light from the printer may be changed.
- 15 While we have described this process and designed it particularly for a colour 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 films.
- 20 The invention is not limited to the preferred form described above by way of example.
- 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 claim is:—
1. Process for the production of a multi-colour photograph from a multilayer film having a layer containing a record of one colour component in silver bromide and another layer composed of silver chloride emulsion containing a record of another colour component, which includes the steps of developing the record in the silver chloride layer and fixing it without affecting the record in silver bromide.
 2. Process for the production of a multi-colour photograph from a multilayer film having a layer on one side of the support containing a record of one colour component in silver bromide and a layer composed of silver chloride emulsion on the other side of the support containing a record of another colour component, which includes the steps of developing the record in the silver chloride layer and treating the film with ammonia to fix the silver chloride layer without affecting the record in silver bromide.
 3. Process for the production of a multi-colour photograph from an exposed multilayer film having one emulsion layer of silver chloride, which includes the step of converting the colour sensation record in another gelatino-silver halide emulsion layer to silver bromide without further exposure so as to permit development and fixing of the silver chloride layer without affecting the silver bromide layer which is to be processed to a different colour.
 4. A film suitable for the production of a multicolour photograph by the process of claim 1 consisting of a single support carrying a plurality of superimposed gelatino-silver halide layers sensitized to different colours of which one at least consists of an emulsion of silver chloride.
 5. A film suitable for the production of a multicolour photograph by the process of claim 2 consisting of a single support carrying superimposed gelatino-silver halide layers on its opposite sides of which at least one consists of an emulsion of silver chloride.
 6. A film for three-colour photography having two layers of silver bromide emulsion sensitized to different colours and a layer of silver chloride emulsion sensitized to a third different colour all superimposed on a single support.
 7. A film as claimed in claim 5 in which a single emulsion layer is carried on one side of the support and consists of silver chloride emulsion.
 8. A film as claimed in claim 7 in which the single layer consisting of silver chloride emulsion is protected by a removable waterproof coating thereover.
 9. Process for the production of a three-colour photograph from a film comprising a support having two superposed differentially colour sensitized gelatino-silver halide layers on one side thereof, and a gelatino-silver chloride layer on the other side sensitized to a third different colour and protected by a removable waterproof coating, according to which the double layer side is processed to produce a coloured image in the lower layer and an unexposed silver bromide image in the upper layer whereafter the waterproof coating is removed from the silver chloride layer, and that layer is processed to another colour, and fixed without affecting the said unexposed silver bromide image, and finally the silver bromide image is exposed and processed to a third colour.
 10. Process as claimed in claims 1, 2 and 9 in which the development consists of colour development.
- Dated this 26th day of June, 1934.
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12, Church Street, Liverpool, 1.
Chartered Patent Agents.



[This Drawing is a full-size reproduction of the Original.]