PATENT SPECIFICATION

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427,519

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(Divided out of No. 427,472)

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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 colour photographic processes and particularly those adapted to colour motion pictures. More specifically it relates to a new or improved multi-layer photographic sensitized film and method of processing the same.

According to the present invention there is provided a multi-layer photographic sensitized film in which the layers are substantially uncoloured but differentially colour sensitized and in which one of said layers is sensitized to infra-red. Thus the sensitized film may comprise a support carrying three substantially uncoloured layers, two of which are colour-sensitized to two different regions of the visible spectrum and the third of which is sensitized to the infra-red region of the spectrum.

According to a further feature of the invention a photographic sensitized film as described above and having two layers sensitized to two different regions of the visible spectrum is processed so that the latent images in these layers obtained as a result of printing through appropriate filters are converted into images in the minus colours corresponding to the colours to which the layers were sensitized. Both layers may be processed to the minus colour corresponding to the colour to which the lower layer was sensitized whereafter the upper layer only is bleached and subsequently processed to the minus colour corresponding to the colour to which it was sensitized.

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

In the drawings:—

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.

As shown in the drawings, this positive film comprises a support 20 having on one side superposed layers 21 and 22 of highly transparent emulsion, the lower 21 being 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.

This positive film may be printed upon 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).

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 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 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 copending 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 of the blue record component with infra-red light. In the resulting positive the record of the red, i.e. of the original red component, is in the top layer and is to be processed to a minus red colour. The record of the original green component is 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 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 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 sensitized to the green region of the spectrum between 510—590 *mμ*, with a maximum at about 550 *mμ*. A fast emulsion sensitized with erythrosin has been found satisfactory. Over this 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 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 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 sensitizer conferring sensitivity primarily in the region between 600 and 700 *mμ* with a maximum near 650 *mμ*. Such a sensitizer is naphthocyanol. Both layers are, of course, sensitive to blue. The red 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, hereinafter 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 *mμ*. For the lower 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 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 latitude, speed, contrast, and maximum density.

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 employed in the colour processing.

These positive emulsions are chosen for 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 waterproof 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.
Toluene	100 cc.
Xylene	400 cc.

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

Although this infra-red-sensitive emulsion may be of the type described for the other two coatings, it is advisable to have it 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 (thiotricarbocyanine).

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. Such a film containing a silver chloride layer, and methods of processing it involving differential fixation, are claimed in our co-pending application No. 18933/34 (Serial No. 427,517).

COLOUR PROCESSING THE PRINTED FILM.

The printed material has a waterproof 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. 18932/34 (Serial No. 427,516), and 18936/34 (Serial No. 427,520).

For the red (minus green) colour developer, we prefer the following solution.

FORMULA II.

Water	1 litre.
Diethyl para-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 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-phenylene-diamine 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 described in our co-pending applications Nos. 18932/34 (Serial No. 427,516) and 18936/34 (Serial No. 427,520).

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 Fig. 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.

If differential fixation in ammonia is inconvenient or impossible (for example when the infra-red sensitized layer contains silver bromide and the image in the upper of the two layers on the other side of the support is bleached to silver bromide) it is necessary to employ methods of flotation or other mechanical means in differentially processing opposite sides of the film. These are practicable and may be used to avoid the necessity of water-proofing one layer with varnish but appear less useful than the one fully described above.

The order of the emulsion layers of the positive with respect to the direction of light from the printer may be changed.

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.

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. A multi-layer photographic sensitized film in which the layers are substantially uncoloured but differentially colour sensitized and in which one of said layers is sensitized to infra-red.

2. A photographic sensitized film as claimed in Claim 1, in which the infra-red sensitized layer is the sole layer on one side of the support.

3. A photographic sensitized film comprising a support carrying three substantially uncoloured layers two of which are colour-sensitized to two different regions of the visible spectrum and the third of which is sensitized to the infra-red region of the spectrum.

4. A photographic film as claimed in Claim 3 in which the two layers colour sensitized to two different regions of the visible spectrum are superposed on one side of the support and the infra-red sensitized layer is on the other side of the support.

5. A photographic sensitized film as claimed in Claim 4 in which the infra-red sensitized layer is covered with a removable water-proof coating.

6. A photographic sensitized film as claimed in Claim 4 or Claim 5 in which a thin layer of clear gelatine is present between the two layers on the one side of the support.

7. A photographic sensitized film as claimed in any of Claims 3 to 5 in which the two layers colour sensitized to different regions of the visible spectrum are sensitized to red and green respectively.

8. A photographic sensitized film as claimed in Claim 7 in which the layer sensitized to green lies between the layer sensitized to red and the support.

9. A method of processing the photographic film claimed in any of Claims 3 to 8, in which latent images produced by printing on the two layers sensitized to two different regions of the visible spectrum through appropriate filters are processed to the minus colours corresponding to the colours to which they are sensitized.

10. A method as claimed in Claim 9 in which the latent images are first processed to the minus colour corresponding to the colour to which the lower layer is sensitized whereafter the upper layer only is bleached and processed to the minus colour corresponding to the colour to which it was sensitized.

11. A method of processing the photographic film claimed in Claim 5 which consists in first processing the two layers superposed on one side of the support to one colour, bleaching the upper layer without exposure and then removing the water-proof coating from the infra-red sensitized layer and processing that layer to a different colour.

12. A method of processing a photographic film as claimed in Claim 11 in which the layer which was sensitized to infra-red is fixed without affecting the bleached layer and finally the bleached layer is processed to a third different colour.

13. A method as claimed in any of Claims 9 to 12 in which the layer sensitized to infra-red is processed to minus blue.

14. A photographic sensitized film comprising a support carrying three differentially sensitized layers, one of which is sensitized to infra-red, substantially as described.

Dated this 26th day of June, 1934.

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Chartered Patent Agents.

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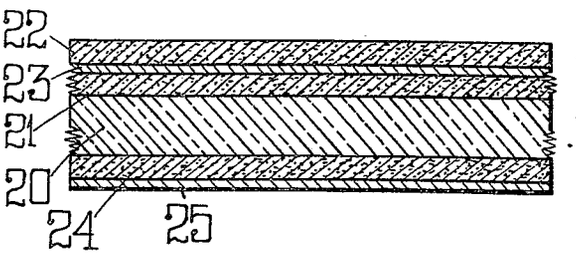

Fig.1.

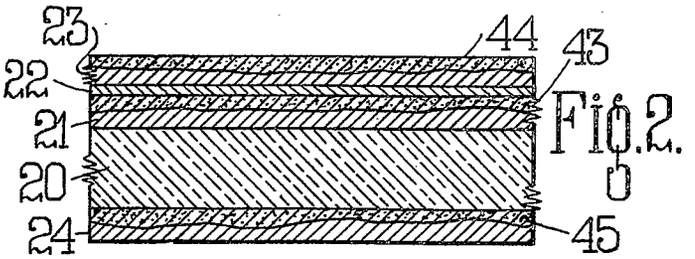

Fig.2.

Malby & Sons, Photo-Lith.