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PATENT SPECIFICATION

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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 in particular to the production of three-colour photographic records especially for colour motion pictures.

In particular, the invention relates to a process of producing a three-colour photographic record which comprises first obtaining a record in two colours of three colour sensations by forming in one area of a first sensitive element having two superposed differentially sensitised layers a latent image in each of one colour component and in another area of said first sensitive element latent images respectively in the two layers of two other different colour components and transforming the latent images in said two layers into coloured images of two different colours, and then forming on a common area of a photographic element three registering, differently coloured images corresponding respectively to each of the three colour sensation records.

According to the present invention, in a process of this kind, there is produced from the record in two colours thus obtained a record in three colours by exposing an area of a second sensitive element carrying three differentially sensitised layers to printing light of three different colours transmitted respectively by the three colour sensation records of the first element, the three colours of light being those to which the layers of the second element are differentially sensitive.

The coloured images of the two different colour components in the one area may be printed on the second sensitive element by a single beam of light of two colours and the coloured image of the other colour component in the other area may be printed by light of a third colour different from either of the two colours in the aforesaid single beam. Thus, three separate colour records of red, green and blue colour sensations may be recorded in a two layer recording material, the records in one layer being minus red and in the other layer minus green so that the red and green sensation records may be printed by a single beam of red and green light and the third or blue sensation record by infra-red light.

A three colour subtractive picture can then be produced by processing the latent images in the respective layers of the three-layer element to the negative colours of the colour sensations from the original object which they represent.

Other features of the invention will be apparent from the following description and the appended claims.

Preferred methods of putting the invention into practice will be described by way of example utilizing the processing methods described and claimed in our copending applications Nos. 18932/34 (Serial No. 427,516), 18934/34 (Serial No. 427,518), and 18936/34 (Serial No. 427,520), and a positive material having features described and claimed in our copending applications Nos. 18933/34 (Serial No. 427,517) and 18935/34 (Serial No. 427,519).

In the accompanying drawings :—

Figure 1 is a diagrammatic cross-section of the negative film used.

Figure 2 is a diagrammatic representation of the film in place in a split-beam two-colour camera.

Figure 3 is a cross-section of the negative material after it is processed.

Figure 4 is a cross-section of the positive film before processing.

Figure 5 is a diagram of the shutter of the printer.

Figure 6 is a diagrammatic plan of the printer.

Figure 7 is a diagrammatic side view of the printer, and

Figure 8 is a cross-section of the positive film after processing.

The operations will first be briefly outlined and will then be fully described. The

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negative film constructed as shown in Fig. 1 preferably consists of a support 1 carrying superposed layers of green- and red-sensitized emulsions designated 2 and 3 respectively having a thin intermediate layer of unsensitized gelatine 4. This negative film F is exposed in a split-beam two-colour camera of the type shown in Fig. 2 which will be more fully described hereinafter. Alternate frames A and B are exposed through suitable filters to yellow (red plus green) and blue light respectively. This negative is then processed by converting the latent image in the layer nearest the support into an image of a minus green colour and converting the latent image in the top layer into an image of a minus red. As shown in Fig. 3 in this colour processed negative the red record image 15 is found in area A in the upper layer coloured a minus red; the green record image 16 is found in area A in the lower layer and is coloured a minus green; the blue record image is found in both layers in area B, the portion 17 in the upper layer being coloured minus red and the portion 18 in the lower layer being coloured minus green.

Colour development, as hereinafter defined, is preferably utilised for forming coloured images when processing photographic elements by the present invention.

The expression "colour development" when used herein 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 colour processed negative is printed by projection upon a new type of positive film which is illustrated in Fig. 4. It comprises a support 20 having on one side superposed layers 21 and 23 of highly transparent emulsion, the lower 21 being sensitized to green and the upper 23 to red light and separated by a thin gelatine layer 22 and on the other surface carrying a layer 24 sensitive to infra-red light protected by a waterproof coating 25. The printing is done by projecting the alternate frames in super-position upon the positive film. The red and green record frame A (taken through the yellow filter) is printed on the double coated side of the positive film through a minus blue filter and through a screen which cuts off the infra-red rays (for example, a dilute copper sulphate or cupric chloride solution) which rays would otherwise affect the emulsion on the reverse side of the film. The blue record frame is printed by light of about 720—850 mμ on the single infra-red sensitive emulsion on the reverse side of the film. This may be done by an optical printer of a known type in which the light passed through the area B of the negative film is brought to the reverse side by means of prisms and mirrors, but we prefer the much simplified method of projecting the light which has passed through the area B of the negative film through the double layer on the front of the positive film and thus on to the layer on the reverse side and we have described herein by way of example a positive film which will permit of this being done successfully. This film and the method of printing will later be described in more detail.

It is to be understood that all the layers described in this specification are more or less blue sensitive and care must be taken to exclude blue rays when these layers are intended to record only light records other than blue.

The result of the printing as described is to print the minus red coloured image 15 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 16 is printed on the green sensitive positive lower layer 21. Both of these colour records are found in frame A of Fig. 3. Frame B is printed by infra-red light on the reverse side of the positive either by projection through the other two layers or by optical means as stated. 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 a three-colour positive shown in Fig. 8 which has been produced from a two-colour negative. The full details of the preferred process will now be described, but it will be clear that modifications are possible within the scope of the invention as defined in the claims.

NEGATIVE MATERIAL.

For the negative a film is used carrying two superposed emulsion layers on the same side of the film base. Between these two emulsion layers is a very thin layer of clear gelatine. The two emulsion layers are differentially sensitized with dyes to light of different regions of the spectrum. In practice the following negative material has been found to give the best results.

The film base 1 is first coated with a layer 2 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 4, clear enough to permit adequate exposure of the green-sensitized layer. The final top coating 3 is of the same order of thickness as layer 2 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 as hereinafter described it is the red dye, if any, which is subjected to the bleaching step such as step 4 of method A.

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 negative motion picture film as orinarily 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 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 hereinafter.

NEGATIVE EXPOSURE.

The film is exposed in a camera of the split beam type which exposes two adjacent frames simultaneously to the same light image. Such a suitable camera is illustrated diagrammatically in Fig. 2. A light from the subject S is transmitted by the special optical system to the film as shown. A rhomb 11 of optical glass has cemented to one face a glass prism 12 which is partially silvered along the face 5, being either of the semi-transparent type or having transmitting or reflecting areas. The face 6 of the rhomb is completely silvered. As indicated by the diagram, this system will give rise to two images, one through the face 5 and one from the face 6, which are transmitted by objectives 7 and 8 through corresponding filters 9 and 10 to the two frames A and B of the negative film F. In the ensuing description we shall call any simultaneously exposed pair of frame A and B respectively. It is understood that any colour selection camera of familiar type may be used and that the exposures of successive frames may be made consecutively instead of simultaneously, provided, however, that each frame is exposed through its appropriate filter.

In the path of the beam falling on frame A is a sharp cutting yellow filter 9, of well known type absorbing practically all the blue light, and transmitting red and green light. As the red-sensitive coating 3 of the negative film is practically insensitive to light between 510—590 mμ it will record through the yellow filter only the red light component of a tri-colour system. The lower green-sensitive layer 2 will correspondingly record only the green component ranging from approximately 510—590 mμ. Owing to the relatively larger exposure required for obtaining two correct differential colour component records on frame A as described, the partial reflecting surface 5 in front of lens 7 should transmit considerably more than one-half the incident light directly to frame A, say 70—80%. The remainder of the incident light is reflected to the surface 6 in front of lens 8 which,

in turn, reflects it fully through lens 8 and through a blue filter 10 absorbing red and yellow. Owing to the natural blue-sensitivity of both emulsion layers, frame B will contain the blue component record of the tri-colour system recorded in both emulsion layers substantially without any differential action. As the blue-sensitivity of these rapid emulsions is very high, full exposure may be obtained using only a relatively small percentage of the total light reflected from the subject photographed. The ratio of exposure of frames A and B will naturally be altered according to the source of illumination and other requirements of the materials actually employed. Filters having the absorption characteristics described are well known.

As the camera mechanism (not shown) pulls down two frames at a time for each exposure, double the normal length of film is used.

This negative sensitive material and the process of exposing it form no part of the present invention.

NEGATIVE PROCESSING.

METHOD A.

STEP 1.

After the negative has been exposed, it is developed and fixed as in ordinary photographic procedure. A developing formula is chosen which produces the minimum of selective hardening of the gelatine where the image develops. Diamino-phenol-sodium sulphite containing a small quantity of sodium bisulphite has been very satisfactory. Such a formula is

FORMULA I.

Diamino phenol	5 grm.
Sodium sulphite	10 grm.
Sodium bisulphite	5 grm.
Potassium bromide	1—4 grm.
Water to	1 litre

When it is desired to reduce the number of steps in processing one may develop the latent images in the film directly in a red colour-forming developer (for example formula III), fix, and then proceed to step 4 below. However, increased exposure seems to be necessary when development is to be carried out by this method and it is therefore preferred to perform the operation of colour development upon actual silver salt images.

STEP 2.

The film is now immersed in dilute potassium ferricyanide to convert the silver images to silver ferrocyanide without local hardening of the gelatine. Silver ferrocyanide produced is very easily reducible back to metallic silver. A suitable bleach is

FORMULA II.

Potassium ferricyanide	10 grm.
Ammonia 28%	10 cc.
Water to	1 litre.

STEP 3.

The next step is the exposure and re-development of the bleached images (actual silver salt images) in a colour-forming developer yielding insoluble monochrome dye images, together with re-developed silver. A red or magenta (minus green) dye is required and has been satisfactorily obtained by using cyanacetophenone or thio-indoxyl with di-ethyl para-phenylene diamine in alkaline solution. The dye chosen should, besides permanence and insolubility, have the following two essential properties, thereby excluding certain of the available red couplers: (1) It should have as sharp an absorption band as possible, to afford an efficient printing image. As this image will be required to print on the green-sensitized layer of the positive film, the dye in this printing image should absorb as efficiently as possible the light in the sensitivity range of the green-sensitive positive emulsion, and at the same time transmit as efficiently as possible all the light in the sensitivity range of the red-sensitive positive emulsion. This minus green dye may, and in practice does, transmit blue light as well, for blue light is excluded altogether in positive printing and therefore plays no part in the printing process. (2) It should bleach easily in the bleaching bath employed and not be restored as dye in the subsequent stop bath used in connection with that bleach. In the example described a chromic acid-bromide-alcohol bleaching bath is employed.

A suitable minus green colour developer is

FORMULA III.

Sodium carbonate	10 grm.
Sodium sulphite	0.5 grm.
Diethyl *p*-phenylene diamine HCl	0.5 grm.
Water to	1 litre.

In 100 c.c. of this solution is dissolved 0.05 grm. of brom-thio-indoxyl.

This colour development of both layers must either be carried to completion or, if stopped before completion, must be followed by a hypo bath to remove any undeveloped silver ferro-cyanide. After washing, the film is dried in order to ensure the best result from the differential treatment which follows.

STEP 4.

The next step is the critical one in the colour differentiation 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 25% water solution containing chromic acid, hydro-bromic 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 IV.

Chromic acid, 10% solution	10 cc.
Hydro-bromic acid 41% solution	3 cc.
Potassium bromide	2 grm.
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 :

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 :

Methanol	400 cc.
Sodium sulphite	20 grm.
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 emulsion coatings.

STEP 5.

The above differential treatment leaves the film with silver plus dye in the lower layer, and silver bromide in the upper layer. Therefore, subsequent immersion in a blue-green (minus red) colour-forming developer, such as dichloro- or trichlor-alpha-naphthol with diethyl-para-phenylene-diamine, causes development only in the top layer where the image is formed of silver bromide. Of course, the film must be exposed to white light at this point to render the silver bromide developable.

A suitable blue-green colour developer is the following :

FORMULA V.

SOLUTION A.

Water	1 litre
Sodium carbonate	10 grm.
Sodium sulphite	5 grm.
Diethyl *p*-phenylene diamine HCl	2 grm.

SOLUTION B.

2 : 3 : 4 trichlor-alpha naphthol	1 grm.
Methanol	150 cc.

For use take

Solution A	100 cc.
Solution B	15 cc.

After development in this bath, the film is then washed.

STEP 6.

The final step in processing the negative is to remove the silver image remaining in both emulsions layers, preferably by potassium ferricyanide and sodium thiosulphate, in combination or as separate baths, leaving a pure minus green dye image in the lower layer and a pure minus red dye image in the upper layer. For this bleach the well-known Farmer's reducer is satisfactory.

The finished film, washed and dried, has on frame A (the red-green differential two-colour record) two colour components 15 and 16 superposed and on frame B (the blue-monochrome record) only one colour component existing actually at 17 and 18 in both layers, but for printing purposes existing in the top layer only, as will be fully explained in describing the positive printing process.

NEGATIVE PROCESSING.

METHOD B.

This method may be used instead of that just described, and while it involves more steps than Method A, it has one advantage in minimizing any tendency to harden the gelatine in the image portions and, therefore, facilitates the attainment of satisfactory balance between the emulsions throughout the useful density range.

The film is developed, fixed, washed, and bleached in potassium ferricyanide to give silver ferrocyanide images in both layers. The film is exposed and the top layer only is re-developed to silver by controlling the penetration of an ener-

getic developer and arresting 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 VI.

Hydro-quinone – –	12.5 grm.
Sodium sulphite – –	19.0 grm.
Potassium hydroxide –	41.0 grm.
Sodium sulphate – –	200 grm.
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 VII.

Sodium bisulphite – –	50 grm.
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 VIII.

Sodium sulphite – –	100 grm.
Amidol– – – –	50 grm.
Sodium sulphate – –	200 grms.
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 VII, just given, will also be satisfactory.

At this stage of the processing, the film contains a developable silver ferrocyanide image in the lower layer and a metallic silver image in the upper layer. Immersion in a minus green colour developer as described under Method A, Step 3, is now carried out, depositing dye along with the silver of the image which is being redeveloped in the lower layer only, the silver image in the upper layer being, of course, inert to the colour developer. This colour re-development of the lower layer may be either carried to completion or followed by a dilute hypo bath to remove undeveloped silver ferrocyanide. The film is now washed. The lower layer now contains minus green dye plus silver; the upper layer contains silver only.

The silver image in the upper layer only is bleached by controlled diffusion of a potassium ferricyanide bath, which converts the silver image to silver ferrocyanide. 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 bleach is

FORMULA IX.

Sodium sulphate – –	200 grm.
Potassium ferricyanide –	50 grm.
Water to 1 litre.	

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 immersion of the film in a dilute solution of hydroxyl-amine hydro-chloride and ammonia which rapidly converts the remaining potassium ferricyanide carried along in the gelatine to potassium ferrocyanide, the latter compound having no bleaching action. Such a suitable stop bath is :

FORMULA X.

Hydroxyl-amine hydrochloride	20 grm.
Ammonia 28% – – –	55 cc.
Water to 1 litre.	

This stop bath is used at room temperature.

Hydrazine or hydrazine sulphate may be substituted for hydroxyl-amine hydrochloride in the above formula.

The silver ferrocyanide image now in the top layer is exposed and developed in a blue-green (minus red) colour-forming developer, as described under Method A (Step 5, Formula V), to which the silver and dye in the lower layer are inert. When development has proceeded sufficiently far, the silver in both layers is simultaneously removed as described for the final step in Method A, Step 6, in potassium ferricyanide and hypo (Farmer's reducer), leaving a pure dye image in each layer. The film is then washed and dried and is in the same state as represented by Fig. 3.

POSITIVE MATERIAL.

On one side of the film base two emulsions are coated with an intermediate, very thin gelatine layer between them. These emulsions are coated respectively in the same order to approximately the same thickness and with substantially the same colour-sensitizing specified for the negative material. Accordingly, there is a

green-sensitive layer 21 next the support 20, then the intermediate gelatine layer 22, and then the red-sensitive layer 23. These positive emulsions, however, are chosen for exceedingly fine grain, fine enough to render the appearance of the double-coated film only faintly opaque. As stated, each of these layers may be colour-sensitized with the same sensitizing dyes used for the negative material. 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 XI.

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 Specifications Nos. 327,714, 339,902 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 (thio-tricarbocyanine).

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.

POSITIVE EXPOSURE.

It will be understood that both frames of the negative film belonging to each simultaneously exposed pair must be printed in register on a single frame of positive film. This may be accomplished in an optical printer of a form known to the art, in which the printing of the two frames is done simultaneously, by simple projection of the image in one frame on to the front of the positive film and projection of the image in the other frame on to the back of the positive film in register by an optical system of several prisms and lenses, a typical printer being shown in Patent Specification No. 13,430/15. In such case any anti-halation backing must be one which transmits the back printing light.

We prefer, however, to carry out this printing by an arrangement which has great advantages of simplicity. This printer is illustrated diagrammatically in Figs. 6 and 7, the shutter being shown in Fig. 5. In this printer both negative and positive films, designated N and P respectively, travel intermittently, the former passing two frames successively past a single gate to every one frame of the positive film exposed at the other gate. Registration is important and may be insured by any of the well known expedients, such as by a uniform spring pressure from one side of each film gate, by accurate intermittent mechanisms, and by registration pins entering the film perforations at both gates while the films are at rest during exposure intervals. Since these are familiar mechanical details, they are not shown in full, as they would tend to complicate the drawing and obscure the salient features.

Frame A of the negative containing two differential colour components is to be exposed by yellow light (red plus green) excluding the extreme red and infra-red, thereby affecting the double coated side of the positive film only. Frame B of the negative containing the single blue record component in both layers (non-differentially), is printed by infra-red light of wave lengths 750—850 mμ thereby printing only on the infra-red sensitive emulsion on the reverse side of the positive film. The positive emulsions are particularly transparent to light of these longer wave lengths, resulting in a minimum loss of definition due to printing through two emulsions and through the film base to the coating on the reverse side.

The varnish backing, when it contains a black dye or lamp black, affords protection against halation. Blue light is excluded from the positive printing as hereinafter described.

In the printer shown diagrammatically in Figs. 6 and 7, two sources of light are employed as shown, each with stationary filters attached. One light source 30 is

on the optical axis of the printer and the other 31 at right angles to it. A special type of shutter 32, shown in Fig. 5, is used, having one sector 33 open except for rim 34 and one reflecting mirror sector 35 opposite the open sector to transmit successively the suitably filtered light from the two light sources 30 and 31 in synchronism with the successive exposures of the alternate negative frames. The other two sectors 36 are opaque and non-reflecting.

The negative film N is driven past gate 37 by a pulldown mechanism shown conventionally at 38 and operating in timed relation with the shutter 32, such that the movement occurs as the opaque sectors 36 pass the optical axis. The positive film P is moved past gate 37 by a pull-down 40 of the type shown in Capstaff U.S. Patent No. 1,672,845, granted June 5, 1928, whereby the claw engages and advances the film only at every alternate stroke. This mechanism is so connected to the pulldown mechanism that it moves the film during alternate movements of Film N.

In front of light 30 is a filter 41, of known type, which may be a combination of layers or dyes, excluding virtually all the extreme red and infra-red as well as blue during one printing exposure, while transmitting at the same time enough visible red and green light for printing the red and green colour components. For excluding the blue light a suitable known yellow filter may be employed. For excluding the infra-red, a filter comprising a dilute solution of cupric chloride has been satisfactorily employed. Less satisfactory for absorbing infra-red, though more convenient, are heat-resisting glasses of greenish colour of well known type, whose absorption in the infra-red is relatively high compared to their absorption in the visible red. Such a suitable liquid filter cell of 1 cm. cell thickness will contain $2\frac{1}{2}\%$ of cupric chloride in water. In front of the other light source 31, the filter 42 will consist of an infra-red filter of known type (i.e. a filter passing only infra-red light) and also a glass or liquid filter to exclude a great deal of the infra-red light of wave lengths longer than 800 mμ. A liquid filter of 1 cm. cell thickness containing $\frac{1}{2}\%$ of cupric chloride is satisfactory for this purpose. The reason for excluding these higher wave lengths is that the blue-green dye used for the printing image in the negative film transmits the longer wave lengths more easily, thereby decreasing its effective contrast in printing.

The type of printer described is used to avoid having revolving liquid filter cells which might otherwise be required. It is, however, possible to design such a printer which would contain a shutter having two open sectors, as heretofore used in printing of this kind, one of the open sectors of the shutter containing one filter and the other the other filter.

The result of the optical printing as described is to print from a minus red coloured image 15 in frame A of the negative film, representing the red record component, upon the red-sensitised top coating 23 of the positive film, a latent printed image which is afterwards processed to a minus red colour. Similarly, from the minus green coloured image 16 is printed in the green-sensitive positive layer 21 a latent image which is afterwards processed to a minus green image. From the blue record components in frame B, is printed by infra-red light in the coating 24 of the positive a latent image which is afterwards processed to a minus blue. The minus red dye image 17 in the top layer of the negative film is also substantially minus infra-red and therefore prints effectively, whereas the minus green image 18 in the lower layer is virtually transparent to the infra-red, and therefore negligible in printing. The result is that each of the three-colour components is printed from one layer only of the negative film and in one layer only of the positive film.

POSITIVE PROCESSING.

The positive has a water-proof varnish layer 25 on one side so that the double layer side only is treated at this point.

The processing of the double layer side of the positive film may be carried out by the same sequence of steps as employed in negative processing by Method A or Method B, without exposure of the infra-red sensitised layer to light to which it is sensitive. We may, however, proceed direct to step 3 of Method A so that the processing comprises the following steps :—

1. Development of the initial latent images in a red (minus green) colour developer.

2. Treatment of the film in a bleach bath which is restricted to the depth of one layer only.

3. Development in a blue-green (minus red) colour developer and

4. Removal with Farmer's reducer of the silver images remaining.

For the red (minus green) colour developer of Step 1, we prefer the following solution for the positive red images :

FORMULA XII.

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 processing then follows steps 4 and 5 of Negative Processing Method A (while, of course, protecting the infra-red sensitised layer from light to which it is sensitive) after which the protective varnish is removed from the layer at the back of the positive and the latent image in this layer developed in a yellow (minus-blue) colour forming developer.

A suitable formula for the yellow colour developer is :

FORMULA XIII.

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, however, possible and available. Besides benzoyl acetones, aceto-acetic esters have been used as couplers with diethyl-paraphenylene diamine as developer.

Thus furnishes the third subtractive positive colour component corresponding to the original blue negative record which, it will be remembered, has been printed by infra-red on the single coating on the reverse side of the positive.

Alternatively, however, we may proceed by steps 1 and 2 above and then, at that stage where the top layer only of the double coating has been bleached to silver bromide and the dye in that layer removed coincidentally, strip the protective varnish 25 from the infra-red sensitive layer 24 on the reverse side while protecting the film from exposure. This varnish is easily stripped when dry. The film is now immersed in a pure yellow (minus blue) colour forming developer, such as Formula XIII above.

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 which may be of the same type as that given in Step 5 of the negative processing Method A.

After all three layers have been developed to the different colours, the positive is thoroughly washed and the silver images remaining in all three emulsions are simultaneously removed as described under Negative Processing, Method A, Step 6. This step involves a simple reduction by Farmer's reducer.

The film is now washed and dried and is a complete three colour subtractive picture, as shown in Fig. 8 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.

Numerous variations in the process as outlined may be made, of which the following are examples :

If the finished processes negative as described above is printed in a contact printer by yellow light on positive material double-coated but without the third varnished infra-red sensitive emulsion on the reverse side, and if it be processed according to either Method A or Method B under "Negative Processing", a master positive will result. Repetition of this process will result in a master negative.

To avoid excessive re-duplication and consequent loss in quality, the master positive just described may be put through an ordinary reversal treatment after exposure and thereafter processed by Method A or B, "Negative Processing", yielding a direct master negative on fine-grained film but otherwise a substantial duplicate of the original negative in every respect.

In making these master positive or master negative prints, it will be of advantage to use as a source of printing light not yellow light but additive red plus green light from two nearly monochromatic light sources which will minimize the loss of colour intensity due to excessive re-duplication.

If differential fixation in ammonia is inconvenient or impossible (for example when the infra-red sensitive 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 var-

nish but appear less useful than the one fully described above.

The colour sensitizing of the layers of the negative may be changed altogether from that described. The sensitivity range may be quite different from that mentioned. The two layers of the negative may be coated in the reverse order. The intervening thin gelatine layer between the two layers of the negative may contain a dye to act as a screen for the layer underneath.

The colours chosen for processing the negative may be changed, as green and red need not necessarily be used. A blue and a yellow, or a blue green and orange yellow, may be used to form efficient printing images, in which case the double coating of the positive described will have two emulsion layers sensitized to blue and to orange respectively, in either order.

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

Owing to the length of the foregoing description, it may be of advantage to summarize the steps of one form of the complete process to which, however, the invention is not limited.

NEGATIVES.

Double coated red and green sensitized film is exposed in a split-beam camera, two frames at a time through yellow and blue filters respectively. This is processed to a minus green. The top layer is then bleached and redeveloped to a minus red. The silver is removed leaving pure dye images. Method A described above is the simplest for carrying out these steps.

POSITIVES.

The film has coated red- and green-sensitive transparent emulsions on one side of the support and an infra-red-sensitive coating on the reverse side, this being protected by a waterproof, stripping, antihalation varnish coating. The positive is exposed one frame at a time for each two negative frames in a special optical printer using red and green light for one negative frame and infra-red light for the other. The double layer is developed to magenta (minus green) and fixed. The top layer is bleached. The stripping layer is removed from the infra-red emulsion which is developed yellow and fixed in ammonia. The bleached top layer on the double coated side is exposed and redeveloped to a blue-green (minus red). The silver in all layers is removed, leaving pure dye images.

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.

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. In a process of producing a three colour photographic record of the kind described, producing from the record in two colours a record in three colours by exposing an area of a second sensitive element carrying three differentially sensitised layers to printing light of three different colours transmitted respectively by the three colour sensation records of the first element, the three colours of light being those to which the layers of the second element are differentially sensitive.

2. The process of producing a three colour photographic record as claimed in claim 1 in which the coloured images of the two different colour components in the one area are printed on the second sensitive element by a single beam of light of two colours and the coloured image of the other colour component in the other area is printed on the second sensitive element by light of a third colour different from either of the two colours in the aforesaid single beam.

3. The process of producing a three-colour photographic record as claimed in claim 1 or 2 in which the two layers of the first sensitive element are sensitised to red and green respectively and a negative record of the blue colour sensation is obtained in both layers of the one area by exposing that area behind a blue screen whilst negative records of the red and green colour sensations are obtained in the respective layers of the other area by exposing that other area behind a yellow screen.

4. The process of producing a three-colour photographic record as claimed in claim 3 in which the negative latent images in the green sensitive layer are processed minus green and the negative latent images in the red sensitive layer are processed minus red.

5. The process of producing a three-colour photographic record as claimed in claim 4 in which the three differentially sensitized layers of the second sensitive element are respectively sensitized to infra-red, green and red light and a record is obtained therein by exposing an area of said second sensitive element to infra-red light transmitted through the area of the first sensitive element which contains the blue colour sensation record and to green plus red light transmitted

through the area of the first sensitive element which contains the red and green colour sensation records.

6. Process as claimed in claim 5, in which the blue colour sensation record is printed on the second sensitive element by infra-red light passed through the red and green sensitized layers.

7. The process as claimed in any of the preceding claims in which the latent images in the respective layers of the three-layer element are processed to the negative colours of the colour sensations from the original object which they represent.

Dated this 19th day of September, 1933.
W. P. THOMPSON & Co.,
12, Church Street, Liverpool, 1,
Chartered Patent Agents.

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[Wt. 8012B.—50/7/1937.]

427,472 COMPLETE SPECIFICATION
2nd Edition

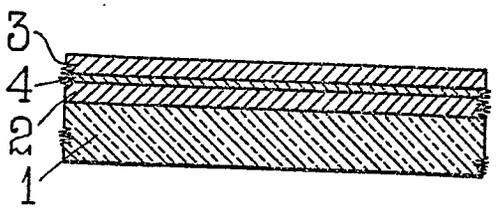


FIG. 1.

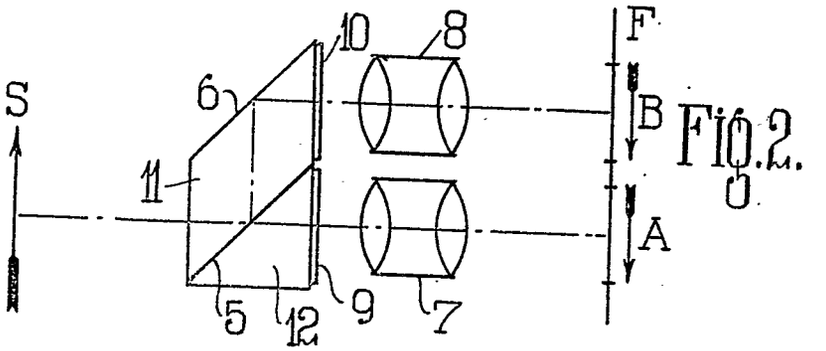


FIG. 2.

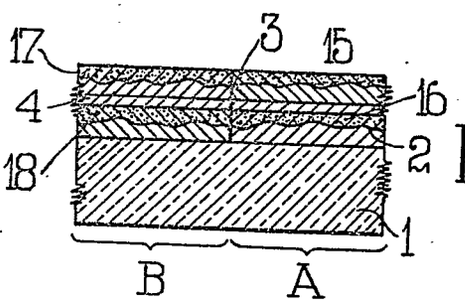
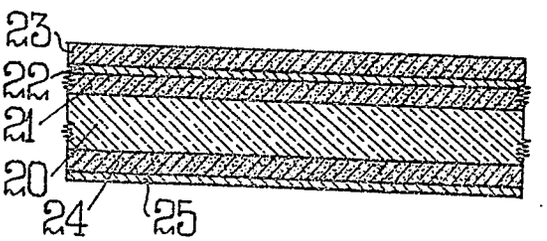


FIG. 3.



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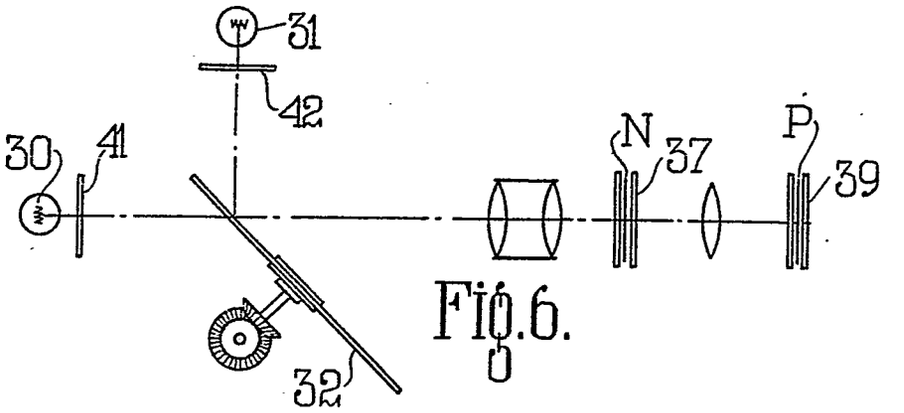

Fig.6.

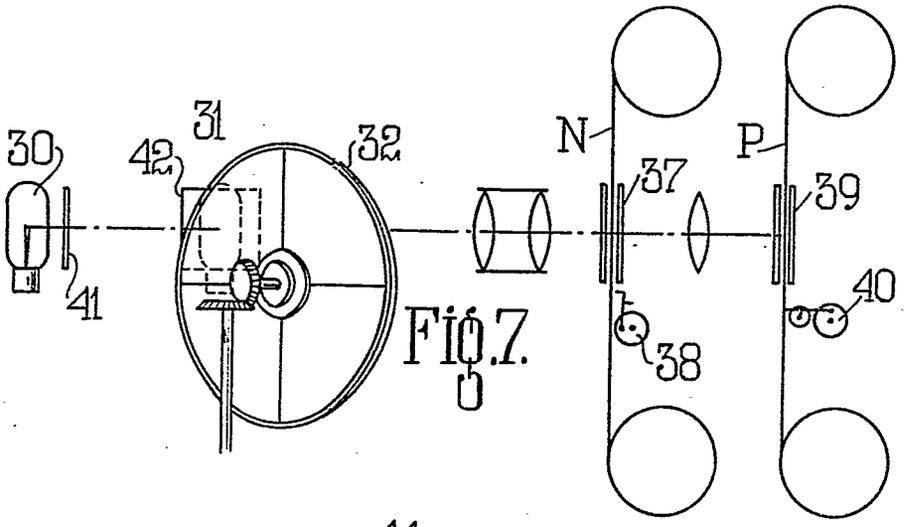

Fig.7.

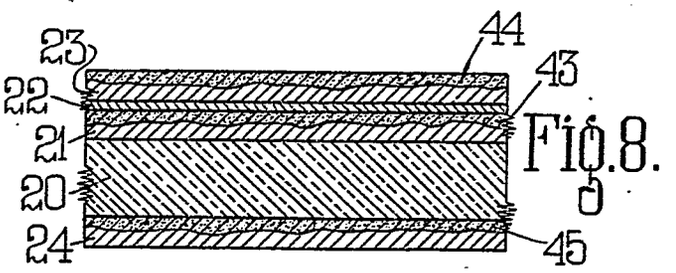

Fig.8.

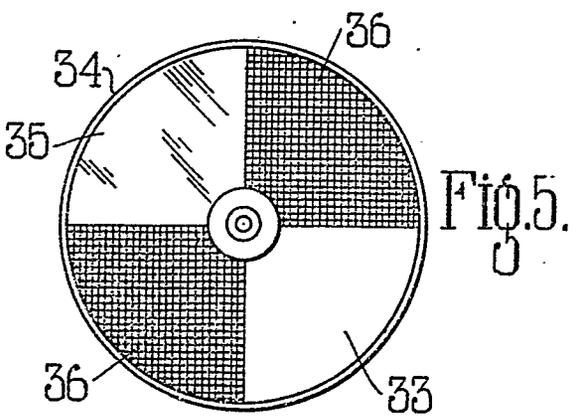

Fig.5.

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SHEET 1

2 SHEETS

SHEET 2

[This Drawing is a reproduction of the Original on a reduced scale.]

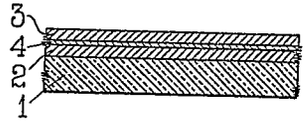

Fig.1.

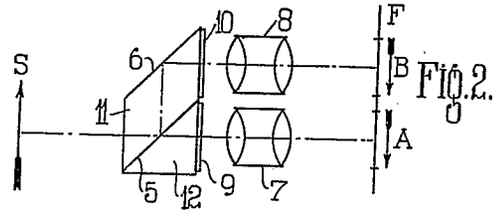

Fig.2.

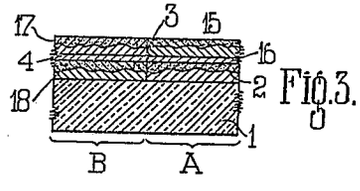

Fig.3.

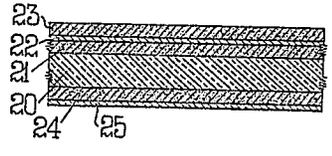

Fig.4.

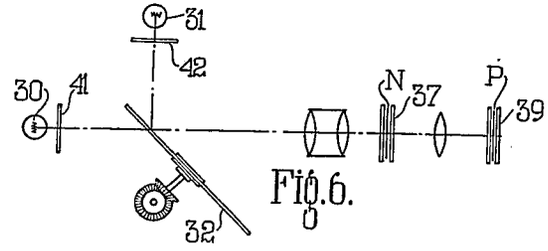

Fig.6.

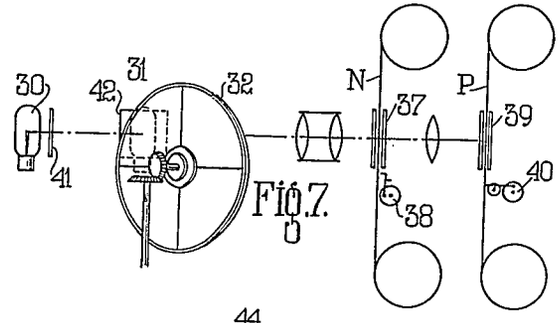

Fig.7.

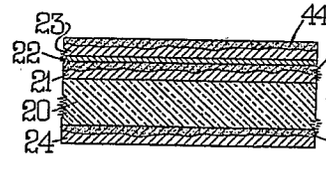

Fig.8.

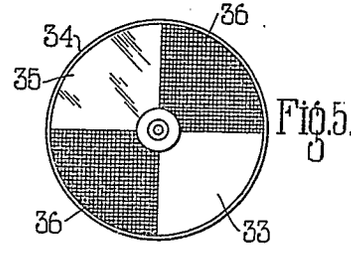

Fig.5.

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