

PATENT SPECIFICATION

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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 photographic processes and particularly those adapted to colour motion pictures.

More specifically the invention relates to new or improved methods of colour processing photographic elements having a plurality of layers containing different colour sensation silver salt records on a single support.

Specification 376,838 describes and claims the method of producing a colour photograph comprising 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 redeveloping 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 redeveloped 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 redeveloped silver of the upper layer or

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layers. The plate, or film, may be fixed in sodium thiosulphate, washed, and then dried, and the remaining layer or layers bleached to silver ferrocyanide for redevelopment in another colour-forming developer, and so on to the third coating in the case of three colour photography. Instead of this method of separation by controlled diffusion of concentrated redeveloper the negative may, according to this prior patent, be treated as follows. The plate or film is developed, fixed and dried. The top layer is converted to silver ferrocyanide by controlled diffusion of potassium ferricyanide in solution. Treatment with a colour developer will then affect this bleached layer only. The silver may be removed from this top image record by controlled diffusion of any suitable silver-solvent. The lower layers are successively treated in this manner using a different colour developer for each until only pure colour remains. Obviously this method depends on controlled diffusion of the potassium ferricyanide employed.

The process of the present invention resembles the process described in the above specification in so far as it results in the formation of colour images in the different layers by bleaching and re-development with developers containing respectively different colour formers but differs from it in features which will be apparent from the following description and the appended claims and which are of substantial importance in the practical production of colour photographs.

According to one feature of the present invention the method of colour processing photographic elements having a plurality of superimposed layers containing different colour sensation silver salt records on the same side of a single support includes colour developing all the silver salt records in the layers to one colour, fixing if necessary and then bleaching the colour developed records in all except the bottom layer to remove and/or destroy the colour and transform the silver which was developed therewith into developable silver salt. The expression "silver salt records" is intended to include latent or

bleached silver images.

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 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 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.

In order to avoid as far as possible bleaching of the bottom layer during the bleaching operation there is preferably provided over the bottom layer a layer of clear gelatine, as set forth in co-pending application No. 18934/34 (Serial No. 427,518) and diffusion of the bleaching agent is arrested before it has penetrated through this clear gelatine layer. This gelatine layer must be sufficiently clear to permit adequate exposure of the sensitised layer therebeneath.

According to a further feature of the invention, the method of colour processing photographic record elements having a plurality of superimposed layers containing different colour sensation silver salt records on the same side of a single support includes colour developing all the silver salt records in the layers, fixing if necessary, and then bleaching the colour developed record in an upper layer to remove and/or destroy the colour and reconvert the silver which was developed therewith into developable silver salt without materially affecting the colour developed record in the layer immediately therebeneath. A layer of clear gelatine is preferably provided immediately beneath the upper layer containing the colour developed record to be bleached, for the purpose indicated above.

It is important in obtaining the best results that the photographic record element is substantially dried before the step of bleaching an upper layer only.

If the colour sensation records are in the form of latent images or if the colour development is not carried to completion,

it is necessary to employ a fixing step before the bleaching operation.

The developable silver salt produced by the bleaching is afterwards colour developed to a colour different from that to which it was previously colour developed. Preferably all the silver salt records in the layers are first colour developed to a red.

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

The invention will be illustrated by the following description of a preferred manner of processing a film which is given by way of example.

The film 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 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.

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

The film base is first coated with a layer of a thickness of the order of .0002 inches of a very rapid emulsion sensitized to the green region of the spectrum between 510-590m μ , with a maximum at about 550m μ . A fast emulsion sensitized with erythrosin has been found satisfactory. Over this emulsion is coated a very thin layer, say between .0001 and .00003 inches, of clear gelatine, clear enough to permit adequate exposure of the green-sensitized layer. The final top coating is of the same order of thickness as the green-sensitized layer 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 700m μ with a maximum near 650m μ . 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 which is subjected to the bleaching step such as step 4.

5 It is important for this red-sensitized layer to use an emulsion that is relatively insensitive to light of wave-lengths between 510 and 590m μ . For the lower
10 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
15 single normal coating on negative 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
20 density.

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

COLOUR PROCESSING.

Step 1.

30 After the film 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.
35 Diamino-phenol-sodium sulphite containing a small quantity of sodium bisulphite has been found very satisfactory. Such a formula is :

FORMULA I.

40 Diamino phenol - - - 5 gm.
Sodium sulphite - - - 10 gm.
Sodium bisulphite - - - 5 gm.
Potassium bromide - - - 1.4 gm.
Water to - - - 1 litre.

45 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
50 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 develop-
55 ment upon actual silver salt images.

Step 2.

The film is now immersed in dilute potassium ferricyanide to convert the silver images to silver ferrocyanide with-
60 out local hardening of the gelatine. Silver ferrocyanide produced is very easily reducible back to metallic silver. A suitable bleach is :

FORMULA II.

65 Potassium ferricyanide - 10 gm.

Ammonia 28% - - - 10 cc.
Water to - - - 1 litre.

Step 3.

The next step is the exposure and re-
70 development of the bleached images (actual silver salt images) in a colour-forming developer yielding insoluble monochrome dye images, together with re-
75 developed silver. A red or magenta (minus green) dye is required and has been satisfactorily obtained by using cyanacetophenone or thio-indoxyl with diethyl para-phenylene diamine in alkali-
80 line solution. The dye chosen, should have permanence and insolubility, and must 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
85 described a chromic acid-bromide-alcohol bleach bath is employed. If this image is required to print on a green-sensitized layer of a printing element, the dye must in addition have as sharp an absorption
90 band as possible, to afford an efficient printing image. The dye in this printing image should absorb as efficiently as possible the light in the sensitivity range of the green-sensitive emulsion of the
95 printing element, and at the same time transmit as efficiently as possible all the light in the sensitivity range of the red-sensitive emulsion of the printing element. This red dye may, and in practice does, transmit blue light as well, but
100 blue light can be excluded altogether in printing.

A suitable minus green colour developer is :

FORMULA III.

105 Sodium carbonate - - - 10 gm.
Sodium sulphite - - - 0.5 gm.
Diethyl p-phenylene di-
amine HCl - - - 0.5 gm.
110 Water to - - - 1 litre.

In 100 cc. of this solution is dissolved 0.05 gm. of brom-thio-indoxyl.

This colour development of both layers must either be carried to completion or, if stopped before completion, must be
115 followed by a hypo bath to remove any undeveloped silver ferrocyanide. After washing, the film is dried in order to ensure the best result from the differential treatment which follows.
120

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
125 depth of one layer only. This is accomplished by subjecting the material to the action of a bleaching bath which penetrates the upper layer and by arresting the action of the bath before it has an
130

opportunity of acting on the lower layer. This can be accomplished by time control of the bleaching operation, employing stop baths to arrest the action of the bleaching agent before it penetrates into the lower layer. Preferably also the bleaching bath contains a loading agent. The use of loading agents in this connection is claimed in our co-pending application No. 18936/34 (Serial No. 427,520) and is not specifically claimed herein. 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, 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 IV.	
Chromic acid, 10% solution	10 cc.
Hydro-bromic acid 41% solution	3 cc.
Potassium bromide	2 gm.
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 gm.
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 gm.
Sodium sulphite	5 gm.
Diethyl p-phenylene diamine HCl	2 gm.

SOLUTION B.	
2 : 3 : 4 trichlor - alpha naphthol	1 gm.
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 film is to remove the silver image remaining in both emulsion 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 film is then washed and dried.

If a negative, processed as described above, is printed in a contact printer by yellow light on printing material double-coated (i.e. without the layer on the reverse side indicated below) and if the printed material be then processed as described, 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 double-coated photographic element may be put through an ordinary reversal treatment

after exposure and thereafter processed as described.

In making 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.

For printing purposes the following material is suitable.

On one side of a 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 next the support, then the intermediate gelatine layer, and then the red-sensitive layer. These printing 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.

The printing material has a layer on the reverse side of the film support comprising a thin coating of slow emulsion, not necessarily transparent, sensitized to the infra-red region from about 750 to 850m μ and covered with a water-proof stripping varnish layer 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 for 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 VI.			
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-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.

Such a film, in which one of the layers is sensitized to infra-red, and features of its processing form the subject of our co-pending application No. 18935/34 (Serial No. 427,519).

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. This feature of the material and of its processing form the subject of our co-pending application No. 18933/34 (Serial No. 427,517).

A method of printing on this material is described in our co-pending application No. 26084/33 (Serial No. 427,472) already mentioned.

COLOUR PROCESSING THE PRINTED MATERIAL.

The printed material has a waterproof varnish layer on one side so that the double layer side only is treated at the outset. 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.

For the red (minus green) colour developer, we prefer the following solution for the printed red images :

FORMULA VII.			
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 bleaching of the upper layer only is then accomplished by the method given in Step 4 of Colour Processing.

At this 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 is removed from the layer 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 VIII.

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

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

Other yellow couplers are, however, possible and available.

15 Besides benzoyl acetones, aceto-acetic esters have been used as couplers with diethyl - paraphenylene diamine as developer.

20 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

30 Colour Processing.

After thorough washing, the residual silver images remaining in all three emulsions are simultaneously removed as described in Step 6 of Colour Processing.

35 This step involves a simple reduction by Farmer's reducer.

40 The film is now washed and dried and is a complete three colour subtractive picture in which the dye images in the three layers respectively successively absorb red, green and blue, and by the subtractive process transmit a properly coloured three-colour image.

45 If differential fixation in ammonia is inconvenient or impossible (for example when the infra-red sensitized layer contains silver bromide and the images 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 described above.

50 The colour sensitizing of the layers of negative material may be changed altogether from that described. The sensitivity range may be quite different from that mentioned. The two layers of negative material may be coated in the reverse order. The intervening thin gelatine layer between the two layers of

65 negative material may contain a dye to

act as a screen for the layer underneath.

The colours chosen for processing negative material 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 printing material to be used therewith will have two emulsion layers sensitized to blue and to orange respectively, in either order.

70 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.

85 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 method of colour processing a photographic element having a plurality of superimposed layers containing different colour sensation silver salt records on the same side of a single support which includes colour developing all the silver salt records in the layers to one colour, fixing if necessary, and then bleaching the colour developed records in all except the bottom layer to remove and/or destroy the colour and reconvert the silver which was developed therewith into developable silver salt.

2. A method as claimed in claim 1 in which there is provided immediately above the bottom layer a layer of clear gelatine and diffusion of the bleaching agent is arrested before it has penetrated through this clear gelatine layer.

3. A method of colour processing photographic elements having a plurality of superimposed layers containing different colour sensation silver salt records on the same side of a single support which includes colour developing all the silver salt records in the layers, fixing if necessary and then bleaching the colour developed record in an upper layer to remove and/or destroy the colour and reconvert the silver which was developed therewith into developable silver salt without materially affecting the colour developed record in the layer immediately therebeneath.

4. A method as claimed in claim 3 in which there is provided immediately beneath the upper layer containing the colour developed record to be bleached a thin layer of clear gelatine and diffusion of the bleaching agent is arrested before it has penetrated through this clear gelatine layer.

5. A method as claimed in any of the 130

preceding claims in which the colour sensation records are in the form of latent images which, after colour developing and before the bleaching operation, are fixed.

5 6. A method as claimed in any of the preceding claims in which the developable silver salt produced by bleaching is colour developed to a colour different from that to which it was previously colour developed.

10 7. A method as claimed in any of the preceding claims in which all the silver salt records in the layers are first produced in colour developed to a red.

15 8. A method as claimed in any of the preceding claims in which a stop bath is employed immediately after bleaching an upper layer, for the purpose described.

20 9. A method as claimed in any of the preceding claims in which a chromium bleach bath is employed.

10. A method as claimed in claim 9, in which the stop bath contains alkali with or without a reducing agent.

25 11. A method of forming two coloured colour component images in registry in two different layers on the same side of a photographic support which comprises forming a colour component developable silver salt image in each layer, colour developing the developable silver salt images in both layers into a silver plus

dye image, subjecting the element for a controlled time to a bleaching bath whereby the effect of the bath is limited to the upper layer and the image therein is reconverted into a developable silver salt image, and colour developing said reconverted silver salt image to a colour different from that of the image in the lower layer. 35 40

12. A method as claimed in any of the preceding claims in which when the images in the layers have been differentially colour developed to the colours required, the silver images are removed from the layers. 45

13. A method as claimed in any of the preceding claims in which a chromic acid-bromide bleach bath is employed. 50

14. A method as claimed in any of the preceding claims in which the photographic record element is substantially dried before the step of bleaching an upper layer only. 55

15. Multi-layer colour photographs whenever prepared or produced by the methods claimed in any of the preceding claims.

Dated this 26th day of June, 1934.

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