

PATENT SPECIFICATION

500,826

Convention Date (Austria) : May 9, 1936.

Application Date (in United Kingdom) : May 10, 1937. No. 13250 / 37.

Complete Specification Accepted : Feb. 10, 1939.



COMPLETE SPECIFICATION.

Process of and Materials for Colour Photography.

We, KODAK LIMITED, a Company registered under the Laws of Great Britain, of Kodak House, Kingsway, London, W.C.2 (Assignees of KARL SCHINZEL, of Ottendorfergasse, 12, Troppau (Silesia), Czechoslovakia, formerly residing in Vienna, Austria, a citizen of the Republic of Austria), 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 improvements in multi-layer photographic elements for three-colour photography and the processing thereof.

The invention relates more particularly to elements having three differentially colour sensitized layers superimposed either all three on the same side or one on one side and two on the other side of a single support. When two layers on the same side of the support consist of the same silver halide they may be constituted by a single coating sensitized in zones for two different colours by allowing a sensitizer to penetrate only superficially into such coating the other layer being sensitized to a third colour.

One object of the invention is to provide photographic elements suitable for recording images corresponding to the three primary colours red, green and blue which images can then be processed to negative or positive images in blue-green, magenta and yellow by operations which do not involve the controlled penetration of processing solutions. These operations involve rendering the respective images which are to be processed to colour, or some of them, developable independently of others. Although this can be done by making use of light filters in the element or colour sensitizers which are resistant to developers and in some cases to mild oxidizing agents (see for example, applications Nos. 26469/38 (Serial No. 501,000), 26470/38, (Serial No. 501,001), 26471/38 (Serial No. 501,002), 33290/38 (Serial No. 500,793), 34976/38, (Serial No. 500,717), and 36871/38 (Serial No. 500,721), of even date) it has been found that the operations are considerably facilitated when one or two of the

differentially colour sensitive silver halide emulsion layers is or are composed of silver chloride, the remainder being silver bromide.

Another object is to facilitate the processing of three-layer elements by operations involving controlled diffusion of processing solutions (see, for example, specifications Nos. 440,032 and 447,092).

In our prior specification No. 427,517 we have described and claimed a process for the production of a multi-colour photograph from a multilayer film having a layer containing a record of one colour component in silver bromide and another layer composed of silver chloride emulsion containing a record of another colour component, which includes the steps of developing the record in the silver chloride layers and fixing it, for example with ammonia, without affecting the record in silver bromide. We have also described and claimed a film, suitable for the production of a multicolour photograph by that process consisting of a single support carrying on the same or opposite sides, a plurality of superimposed gelatino-silver halide layers sensitized to different colours of which one at least consists of an emulsion of silver chloride. We have also described and claimed a film for three colour photography having two layers of silver bromide emulsion sensitized to different colours and a layer of silver chloride emulsion sensitized to a third different colour all superimposed on a single support. The film described by way of example, had two superimposed silver bromide emulsions on one side of the support and a single silver chloride emulsion sensitized to infra-red on the other.

In the elements of the present invention, as will appear more clearly from the following description and appended claims, there is always a silver bromide emulsion layer on the same side of the support as a silver chloride layer.

According to the present invention there is provided a colour photographic element, especially a film, having three differentially colour sensitive silver halide emulsion layers either all three on

[Price

one side or one on one side and two on the other side of a single support, one or two of the three emulsion layers on the same side of the support, or one of the
 5 two emulsion layers on the one side of the support, as the case may be, being silver chloride and the remainder silver bromide. Thus the middle layer may consist of silver chloride emulsion and
 10 the other layers consist of silver bromide emulsion, the layers being on the same or different sides of the support. Alternatively the upper layer may consist of silver chloride emulsion and the
 15 other layers of silver bromide emulsion, the middle layer being on the same side of the support as the upper layer. It is also useful, in some cases, for the upper and lower layers to consist of silver
 20 chloride emulsion and the middle layer of silver bromide emulsion.

The advantage of having a silver chloride emulsion and a silver bromide emulsion in the same element for recording
 25 different colour sensations is that silver chloride can be reacted upon selectively by baths which reduce silver halide or convert it into another silver salt. Thus, if a silver chloride emulsion and a silver bromide emulsion have both
 30 been exposed, or treated with fogging agents, the silver chloride can be developed by a weakly-acting developer which may be a colour developer without development of the silver bromide which
 35 is in contact with the same developer. By "fogging agents" when used herein we mean not only the generally used thiourea but also other known agents
 40 such as thiosinamine, stannous salts, arsenites, hypophosphites, zinc chloride, triaminophenol, thalious salts or fogging dyes which may be used in conjunction with heavy metal salts. It is even
 45 possible, by means of very mild reducing agents, to make the unexposed silver chloride developable without making the unexposed silver bromide developable.

In our application No. 37123/38 (Serial
 50 No. 500,796) of even date we have described and claimed a process of colour photography involving the selecting colour development of silver salt colour component images in
 55 three photographic emulsions on a single support in which one or two of the images only are made developable by treatment with fogging agents after colour development of the images in the other two emulsions or of the image in the remaining emulsion. It will be apparent that
 60 use may be made of that process in the processing of elements constructed according to the present invention whenever a single remaining undeveloped
 65 layer is to be made developable or two

remaining undeveloped layers are to be rendered developable.

Silver chloride is also more readily converted than silver bromide into
 70 coloured substances and mordanting bodies or into silver ferrocyanide.

Another way of taking advantage of the more ready reducibility of silver chloride as compared with silver bromide
 75 is to develop the exposed silver bromide with a colour developer containing alkali carbonate which does not attack unexposed silver chloride, which silver chloride is, however, sufficiently reactive
 80 to be capable of reduction by prolonged treatment with colour developers containing ammonia or caustic alkali or alcohol or acetone (preferably in absence of air) even without exposure or pre-treatment with fogging agents.
 85

Thus in one method of colour processing a photographic element having a silver chloride layer between two silver bromide layers, according to this invention, after general development, the residual silver bromide in the
 90 outer layers is selectively exposed and colour developed (for example by the processes described and claimed in Applications Nos. 24629/38 (Serial No. 498,869), 24630/38, (Serial No. 498,870), or 24631/38 (Serial No.
 95 498,871), of even date) with weakly-acting colour developers and then the residual silver chloride of the middle layer is colour developed by prolonged treatment with a strongly-acting colour developer, for example by the
 100 process described and claimed in application No. 35101/38 (Serial No. 498,875).

Alternatively, after colour processing of the silver bromide emulsions, the silver chloride can be converted into silver
 105 ferrocyanide, and further into red nickel dimethylglyoxime or into yellow titanium ferrocyanide, which latter yields a green-blue image with blue basic dyes. The silver ferrocyanide originating from the
 110 silver chloride can also be converted into other suitable non-tanning mordanting bodies, which are coloured purple or green-blue by basic dyes and may also be removed after insolubilization of the
 115 dyes in order to attain greater transparency.

Generally speaking, in taking photographs of natural objects it is advisable to employ an
 120 element having three superimposed layers of which the upper or middle layer is composed of silver chloride, especially with film coated on both sides where the film itself or a coated filter layer contains colourless substances absorbing ultra-violet (as described and claimed in application No.
 125 34976/38, (Serial No. 500,717), of even date) and the red-sensitive silver halide layer is alone on one side, because under the circumstances silver chloride
 130

develops to colour, if it has not been exposed, and not much silver bromide is attacked.

5 The methods for selective processing of the reversed images in a three-layer element described and claimed in our co-pending applications Nos. 26469/38 (Serial No. 501,000), 26470/38, (Serial No. 501,001), 26471/38, (Serial No. 501,002), 33290/38, 10 (Serial No. 500,793), 34976/38 (Serial No. 500,717), and 36871/38 (Serial No. 500,721), of even date, hereinbefore mentioned, can, of course, also be used when one of the layers consists of silver chloride. In addition to 15 these methods, however, numerous other colouring methods are possible with a three-layer element containing a silver chloride layer, as can be seen from the following examples in which it is assumed that the upper layer is not specially sensitized and the 20 lower layer is sensitized to red :

1. The latent images are developed to silver in all the layers. If the upper layer is the only one which consists of silver chloride, the lower layer is exposed to red light from the back and developed green-blue. Then, either

30 (a) The residual silver halide in the upper and middle layers is simultaneously exposed to ultra-violet rays, and first the silver chloride layer colour developed, then the middle silver bromide layer colour developed, or

35 (b) All metallic silver is removed and then the upper and middle layers are simultaneously exposed from above to blue or white light. By the successive action of weak and strong colour developers, first the silver chloride layer alone and then the middle silver bromide layer are developed in colour.

40 The same procedure is adopted, if the silver chloride layer is in the middle and no yellow filter exists. If there is a filter in the upper layer or between the upper and middle layers one can, after exposing 45 the lower layer to red light and developing it blue-green, next expose the upper silver bromide layer to blue light and develop to colour, then, without previous removal of the reduced silver, 50 develop the middle layer purple with a strongly alkaline colour developer.

55 2. The latent image in the silver chloride layer only is developed to silver with a weak ordinary developer followed immediately by development of the residual silver chloride with a weak colour developer which does not attack the exposed silver bromide. The residual silver chloride may also be directly or 60 indirectly converted into a coloured substance or a mordanting body as described in detail later. After such treatment of the residual silver chloride, the two silver bromide layers are simultaneously developed in an ordinary developer, and

70 finally, the residual silver halide images in these layers are developed successively to the appropriate colours ; this latter can be done by first exposing the layer which was situated away from the objective to light to which it is selectively sensitive and colour developing it and then colour developing the other layer without exposure by means of a vigorous colour developer. 75

This second method can also be employed if the silver chloride layer is in the middle and is especially useful for films coated on both sides.

3. The use of a silver chloride layer in the middle permits all three component images to be independently developed even when no filter layer or only one is present, and the sensitizers are not even stable to an ordinary black developer. 80 85

(a) The latent image of the middle silver chloride layer is first developed alone with a weak ordinary developer. The residual silver chloride image is developed with a colour developer which 90 is just strong enough to reduce the unexposed silver chloride, but not the exposed or unexposed silver bromide. For this purpose the residual silver chloride of this layer could be pre-treated with 95 solutions of very mild reducing agents or compounds containing sulphur which make the residual silver chloride of the middle layer developable, but not the unexposed silver bromide. Since the 100 middle layer is entirely permeated by metallic silver, the two other layers can be independently exposed to blue light after ordinary development, and their residual silver bromide can be 105 individually developed in colour.

(b) After simultaneous development of all three latent images to silver, the residual silver chloride of the middle layer is converted into silver ferrocyanide 110 and this into yellow titanium ferrocyanide or into any other non-tanning coloured insoluble ferrocyanide, or also through nickel ferrocyanide into nickel-dimethylglyoxime, or any other insoluble 115 coloured and easily split complex compound which acts as a screen in the middle permitting individual exposure of the residual silver bromide of the two outer layers. The insoluble ferrocyanides are split by sodium carbonate or 120 alkali, and the complex salts mostly by acids. The silver chloride incidentally formed can be reconverted into silver bromide by means of bromides since silver bromide formed in this way is only very 125 slightly sensitive to light in comparison with the silver bromide of the lower layer. After colour development of the two outer layers, the regenerated silver 130

bromide of the middle layer is made developable by intensive exposure to ultra-violet or X-rays, and developed in colour or developed directly with a vigorous colour developer into the component colour image. Finally, all the silver and the insoluble ferrocyanides are removed and the filter dyes washed out.

(c) The latent images in all three layers are developed simultaneously and the residual silver chloride converted into silver ferrocyanide and this reconverted into silver chloride. This silver chloride obtained by reversion is more highly dispersed than the original silver chloride and is therefore sufficiently easily developable, to enable the middle component image to be developed by a colour developer without exposure. When this has been done the other component colour images are then developed from the residual silver bromide of the two outer layers.

(d) The latent images in all the layers are developed and the residual silver halide of all three layers is made developable simultaneously by ultra-violet or X-rays, and the silver chloride of the middle layer developed alone in colour, by a weakly-acting colour developer so that a homogeneous silver filter is created in the middle. The latent developing ability of the residual silver bromide is now destroyed by the action of mild oxidizing reagents, of *p*-phenylenediamine and acid, or of other known sensitivity destroying agents and sufficient general light sensitivity then created by a bath of alkali sulphite or bisulphite, or a hydrazine or hydroxylamine salt or colour sensitivity created by bathing in known colour sensitizers, preferably in weak ammoniacal solution. The two outer emulsions are then individually exposed (taking advantage of the screen of silver in the middle layer) and developed in colour.

(e) If the middle emulsion is still sufficiently yellow-green or red-sensitive after ordinary development of the latent image in the silver chloride layer alone, it is exposed to the proper light and the residual silver chloride developed in colour so that a homogeneous silver filter also results. The latent images are then developed in the two outer silver bromide emulsions, and finally, their residual silver bromide individually exposed and developed to the corresponding component colour images.

(f) Since a yellow filter between the upper and middle emulsions is indispensable for nature photography, then if such filter is resistant to the first developing agent and silver-removing agents, all

the reduced silver can be removed after general black development of all three emulsions, and then the middle and lower emulsions are simultaneously exposed to blue light, next the residual silver chloride is colour developed with a weakly-acting colour developer, then the residual silver bromide is developed in colour, and finally, the component colour image developed in the upper silver bromide emulsion. The residual silver bromide in the upper layer can be exposed and colour developed before the other two layers. The silver is removed at the end.

The use of silver chloride is especially advantageous with films coated on both sides, on one side with a blue sensitive silver chloride emulsion, and underneath this a silver bromide emulsion sensitized for green-yellow or red-orange, and on the other side a silver bromide emulsion sensitive to red or yellow-green. After general black development and, if desired, removal of the reduced silver and also full exposure of all residual silver halide, each side is developed independently of the other, the residual silver chloride of the double-emulsion-coated side is developed in colour, then the silver bromide of the middle emulsion or middle zone below; finally, the silver bromide emulsion on the other side, or vice-versa, followed by removal of all reduced silver. Instead of a second full exposure pre-treatment with thiourea, or other fogging agent can be employed, or the reduced silver may be removed entirely or for the greatest part, and both sides exposed to ultra-violet rays.

In the greater part of the above description, it has been assumed for convenience, that the red-sensitive emulsion is in the bottom layer. The red-sensitive emulsion may, however, be in the middle layer and the colour processing must then be correspondingly modified. Thus, if the silver chloride emulsion is on top, one can expose to yellow light from the back, after general development (assuming that the sensitizer of the bottom layer has resisted this development) and the lower purple image can then be produced by development. The upper and middle emulsions are then made developable, after preliminary removal of the reduced silver of at least this emulsion, by exposure to white or blue light from above. The yellow component image is then produced in the upper emulsion with a colour developer which acts only on silver chloride, then the green-blue component image in the middle emulsion with a vigorous colour developer.

In the above description, the silver

- chloride layer formed one of three separately coated layers in a triple-layer element. It may, however, form one of two coatings in what may be termed a "two-zone double-layer" element. In such an element two emulsions are independently coated but one of them is made sensitive in different ones of its thickness to two different colours.
- One of the emulsions is sensitized or not in the usual manner, the other one is sensitized in zones for two spectral bands with sensitizers which penetrate only superficially into the coating on account of their colloidal character in dilute alcoholic solution. Examples of such sensitizers will be found in German patents Nos. 471,508; 468,980; 523,074; 528,713; Kinotechnik 1930/476; 1932/264; Jahrb. f. Photo. 1910/367; 1905/185 and Photo. Ind. 1936/433. A yellow or red-orange filter may be placed between the two coatings. The coatings can also be arranged on both sides of the film. The following examples may be cited from the great number of possible means of execution.
- The silver chloride layer may constitute either the upper or lower layer of this two zone double-layer. In one example a thin silver chloride-gelatine- or collodion-emulsion of normal or reduced silver content, highly sensitive for blue, and preferably containing an easily decolourized yellow filter dye, is first coated on the film support. This is followed by a silver bromide gelatine emulsion of normal or less than normal thickness, containing erythrosin or other yellow-green sensitizers in the emulsion. Then it is best to allow a dilute alcoholic solution of pinacyanol or other high-colloidal red sensitizers to act on this layer, preferably after drying. This sensitizes the extreme outer portion of this layer also for red. A pure alcoholic solution of pinacyanol, or other red sensitizer, or one diluted with 10—30% of water can also be allowed to act on the dry layer; or the swelled or previously hardened layer is sensitized with a pure alcoholic solution superficially applied with brushes, rollers or sprays. Exposure is made through the support.
- In the two-zone double layer system, the procedure is generally the same as for the normal triple layer.
- Generally speaking colour development is used for all the images but the residual silver chloride could, of course, also be converted into the yellow component image according to one of the methods described earlier, preferably after development of the middle purple image.
- In the three-layer film the red or yellow-green sensitive silver halide emulsion layer can be situated alone on the back of the support, and the two others on the front. In these films coated on both sides, the support may be very thin, if the motion picture camera is of the continuous moving film type, and development is done under conditions which prevent strong swelling of the preferably moderately tanned gelatine layers. This is attained by addition of alcohol or salts which prevent swelling, such as sodium carbonate or sodium sulphate, to the different baths, also by the use of developers containing a large quantity of alcohol, if the dye generated is insoluble in it. In a three-layer plate, the lower layer (and in films coated on both sides, the middle layer) can consist of silver halide collodion emulsion, or an emulsion of silver halide in any other non-aqueous vehicle. With two layers coated on different sides of the film, both may consist of silver halide collodion emulsion. In order to keep the pores of the collodion open, a layer of gelatine, dextrine, gum arabic, or other water soluble colloid is coated over it, serving at the same time as an anti-halation layer. Thin films of cellulose acetate, regenerated cellulose, or synthetic colloids, lacquered on both sides, if necessary, serve as support. A very thin film, emulsion coated on both sides is temporarily mounted, if necessary, on permeable paper or aluminium foil; for larger images, thin regenerated cellulose or transparent paper, possibly glued on stronger paper, may also be used.
- In films coated on both sides, all previous and subsequent methods of three-colour reversal development and re-development, as well as of the primary three colour development and combination processes, can be made much simpler. Since, in such an element, the double layer consists of a silver chloride and silver bromide emulsion, the residual silver halide of all three layers can be made developable by treatment with thio-urea or other fogging agent. The silver chloride emulsion alone is first developed in colour, then the two other silver bromide emulsions independently of each other.
- If an upper silver chloride and a middle silver bromide emulsion are on the same side of the film and the last silver bromide layer is on the other side, only the silver chloride emulsion is first developed after exposure with a colour developer which is sufficiently weak to act selectively on the silver chloride. The residual silver chloride is converted into silver bromide (which, as stated herein-

before, is much less sensitive to light when obtained in this way than the silver bromide emulsions), then the silver bromide layer, and independently the emulsions of the other side, are each developed to the corresponding component colour images, followed by removal of the silver in Farmer's solution. A yellow filter is inserted between the upper and middle emulsions; the middle layer is sensitive for yellow-green, the lower for red alone. The middle layer adjacent to the support may consist of silver chloride gelatine emulsion, or collodion emulsion.

A silver chloride emulsion is also very suitable for use when two layers are tanned as described in Application No. 24633/38 (Serial No. 499,185).

A silver chloride emulsion can also be used as one layer in an element in which advantage is taken of the possibility of differentially treating the layers by virtue of different degrees of dispersion of the reduced silver. Thus, a blue-sensitive emulsion of highly dispersed silver chloride may be on top, a highly dispersed yellow-green-sensitive silver bromide emulsion in the middle, and a coarse-grain red-sensitive emulsion at the bottom, all untanned. After exposure, the blue-sensitized silver chloride emulsion is developed directly with a very weak colour developer. The highly dispersed silver bromide of the middle emulsion is now developed in colour with a stronger developer and then the coarse-grain silver bromide with a colour developer of normal composition.

An ordinary negative or positive film is painted over with the dilute-alcoholic solution of a yellow-green sensitizer, washed, and then the second layer containing a non-diffusing red sensitizer is coated. The film must, of course, be exposed through the back.

An emulsion layer sensitized by erythrosin, rhodamine B, or one of the thio-pseudo-cyanines, is coated on a non-sensitized silver halide gelatine or collodion-emulsion layer. A yellow filter may be arranged between them, or the lower layer itself may be coloured yellow. The extreme portion of the upper layer is then sensitized for red with pinacyanol in dilute-alcoholic solution, or with another sensitizer which under the proper conditions acts only superficially. The results are, of course, only approximate, because the upper layer is also sensitive for yellow-green. It is, therefore, recommended to eliminate a part of the yellow green sensitizer previously by superficial action of alcohol or acetone, and then to sensitize for red. Orange-red colouring

of this layer serves a similar purpose, since in the superficially treated portion, principally only the red, and towards the middle, only the yellow-green rays act during exposure through the back.

The present invention is also useful in combining re-development with primary three colour development. In films coated on both sides, one of the two emulsions on one side, usually the upper one, consists of silver chloride which can be primarily developed in colour, followed by black development of the other two layers. A silver chloride layer in an ordinary triple layer, preferably in the middle, can be primarily developed in colour, followed by black development of the other two layers. These two latter are re-halogenised after fixing and developed individually by selective re-exposure taking advantage of the presence of a yellow filter to enable the different layers to be selectively exposed from the two sides, or of a remaining yellow sensitivity in one layer to enable this layer to be exposed by yellow light.

The use of the invention in conjunction with controlled diffusion is indicated in the following description.

If approximate diffusion of the reagents by layers is accomplished in the method of direct or reversal colour development or three-colour re-development described before, then under favourable circumstances still more perfect results can be obtained than without these measures and better than can ever be attained by controlled diffusion alone. The main advantage lies, however, in the fact that developer-stable and oxidation-stable sensitizers are, as a rule, not required. The following examples are selected from the great number of possible combinations:—

If the blue-sensitive silver chloride layer is arranged at the bottom, it is exposed or printed through the back and generally developed black.

The residual silver chloride is then directly developed yellow and then the silver bromide of the upper layer is exposed and developed in colour with a surface developer. Finally, the purple component image is developed directly with a vigorous developer in the middle layer. If the middle layer is surrounded on both sides by colour filter layers, a surface development is unnecessary, even if only a red-orange filter is between outer and middle layer, but a yellow developer is used which reduces unexposed silver chloride, but not silver bromide.

If both upper layers consist of sensitized silver chloride, in primary three-colour development the middle silver

70

75

80

85

90

95

100

105

110

115

120

125

130

- chloride layer can be developed in colour with a developer acting only on silver chloride, after superficial colour development of the outer silver chloride layer, then the lower silver bromide layer can be independently developed. In reversal development, it is unnecessary to make the residual silver halide of each layer in succession developable by means of light. It is sufficient to make the residual silver halide of all three layers together developable by exposure, or better still, by pre-treatment with thiourea or other fogging agent or, under certain circumstances, to use those colour developers which reduce also the unexposed silver chloride and silver bromide.
- If a very large aperture lens is available, it is best to arrange a silver chloride emulsion in the middle which by high-sensitization for yellow-green or red-orange becomes just as sensitive as a highly dispersed silver bromide emulsion coated above it which is sensitized to blue. In the reversal process, the residual silver chloride of the middle emulsion alone is developed to the coloured component image after general black development, the upper component image by surface development after general exposure, and finally the lower layer with an ordinary colour developer.
- A similar result can be obtained with a triple layer having a silver bromide gelatine emulsion only in the middle, above and below, however, silver chloride emulsions, preferably with intermediate gelatine layers acting as filters or not. Other colloids less permeable to water than gelatine can be used for the latter and also for the middle silver bromide layer. The possibility of making the middle layer of silver bromide can be used to advantage in two ways, as the following examples show:—
- A colour developer acting only specifically on silver chloride is allowed to penetrate superficially, but deep enough to develop completely the latent light impressions of the upper component colour image. The lower component colour image is then developed by the prolonged action of another colour developer specific for silver chloride, finally, that of the middle silver bromide emulsion.
- The silver is then removed with Farmer's reducer. In the three-colour reversal process, the procedure is similar; after general black development, the upper component colour image is produced by means of a surface developer acting only on the residual silver chloride, then the lower image is produced with a colour developer of normal composition specific for silver chloride, and finally the middle image with an ordinary colour developer, after previously making the residual silver bromide, which has been partially exposed in the second exposure of the upper and lower emulsions, thoroughly developable by thiourea or other fogging agent. The residual silver halide of the lower and middle layers can also be made simultaneously developable by thiourea or other fogging agent, before or after development of the upper layer. After this, the silver chloride alone is developed to the corresponding component colour image and then the silver bromide.
- As already pointed out, the employment of fogging agents in this manner is claimed in Application No. 37123/38 (Serial No. 500,796), of even date.
- If films coated on both sides serve in the above described processes, then after the double emulsion-coated side is developed in colour by surface development by controlled diffusion, the development of the two other layers can be effected independently from that of the other side.
- The method of controlled diffusion can be used to advantage, especially for one component image in the two-zone double-layers, since here stability of the sensitizers is only incidental.
- For example, a thin blue-sensitive and possibly yellow-coloured silver chloride gelatine or collodion emulsion of normal or reduced silver content is coated on the support, over this a silver bromide gelatine emulsion of normal thickness sensitized to yellow-green in the emulsion; a dilute-alcoholic solution of pinacyanol or other red-sensitizers of high-colloidal character is allowed to act on this, preferably after drying, so that the outer zone is sensitive also for red. The exposure is done through the back of the film. Only the upper zone is first developed to the green-blue component image with a dilute-alcoholic developer, if desired after the addition of salts which prevent swelling, then the silver chloride emulsion is developed to the yellow component image under the same conditions as previously mentioned; this is followed by conversion of the still unexposed silver chloride into silver bromide, and finally, by development of the latent image in the middle zone with a weakly alkaline purple developer.
- A silver chloride emulsion made red-sensitive by pinacyanol, or other red-sensitizer, may also be at the bottom, above it a thicker silver bromide emulsion mixed with eosine and a yellow pro-

protecting dye, so that its lower half mainly records the yellow light and the upper extreme outer zone mainly the blue light. The upper component image is first developed with a yellow developer penetrating only superficially, then the lower with a green-blue developer acting only on silver chloride, and finally, the middle one with a purple developer of normal composition, possibly, after conversion of the residual silver chloride into silver ferrocyanide.

A not specially sensitized silver chloride emulsion can also be coated on a thicker silver bromide emulsion sensitized by pinacyanol, or other panchromatic sensitizer and mixed with a blue-violet dye. The former is first developed yellow alone, dried, if necessary, and a colour developer is then allowed to diffuse only so far that only the middle image is developed purple. Finally, the lower emulsion is developed with a blue-green developer and the silver removed with Farmer's reducer.

A silver chloride layer is of great advantage where the coloured image is to be processed by conversion processes. The formation of the middle purple or blue-green component image in a three-layer element offers difficulties which are dealt with by the foregoing methods. Conversion processes permit direct conversion of silver halide into coloured substances or into mordants for basic dyes, or even into precipitants for acid dyes. The latter, however, are less suitable, as acid dyes tend to stain the gelatine intensely and cannot be washed out of the clear places as easily as basic dyes. Most of these methods are very easy to execute, if the middle layer consists of silver chloride whose residual component can be converted into the colour substance directly or through ferrocyanide previously formed, whilst the residual silver bromide is less able to react. It is, therefore, very advisable to remove all the metallic silver after completion of the two other component colour images, to reduce the silver bromide of the middle emulsion and to convert into silver ferrocyanide by means of potassium ferrocyanide, or a mixture of silver ferrocyanide and lead ferrocyanide, by means of one of the known lead intensifiers which is best weakly acidified with acetic acid.

Other methods for production of the upper component colour image are to be considered.

During conversion of the silver chloride, one should take into consideration whether it is located in the upper or middle layer. Conversion before development of the other two emulsions must be

done only if the colour body formed from the silver chloride resists development. This conversion is usually only done afterwards, and is most certain with an upper silver chloride emulsion. If two silver chloride layers are provided, one can be colour developed after exposure, and the other converted alone into the corresponding component colour image by a conversion process.

Suitable conversion products are the following:—

COLOUR FERROCYANIDES.

Prussian blue can be formed in the middle layer, as can red uranyl ferrocyanide, but since this tans too strongly, it is more desirable to form copper ferrocyanide. Yellow titanium ferrocyanide or vanadyl ferrocyanide can be produced in the upper layer, preferably only after preliminary removal of all silver of the two lower layers. Through exposure from the black, the strongly tanning uranyl ferrocyanide can be formed in the upper, yellow-green sensitive emulsion.

COLOURED COMPLEX COMPOUNDS.

Red nickeldimethylglyoxime can serve as the substance for the middle component image. It is formed by the action of a solution of dimethylglyoxime on nickel ferrocyanide formed from silver ferrocyanide and nickel chloride. The higher homologues are also suitable. The silver ferrocyanide formed from silver chloride can react, after conversion into suitable ferrocyanides of other metals and under proper conditions, by means of their chlorides or bromides, also with other complex-forming organic compounds, the same holds true for the lead ferrocyanide formed directly with the lead intensifier, in case complex salts are formed during the reaction, which are less soluble than the corresponding metal ferrocyanide.

Also the coloured mercaptides described in Application No. 30655/38 (Serial No. 500,716) of even date, can be used.

ANTIDIAZOTATES.

A large selection of colour tones is offered by conversion of the residual or regenerated silver chloride or silver ferrocyanide formed from it, as well as of lead ferrocyanide into the corresponding antidiazotate by reaction with alkali antidiazotate. The corresponding diazonium salt, which easily combines with coupling components to give an insoluble azo dye, is formed from silver antidiazotate by the action of acid, after which the resulting silver salt can be removed with thiosulphate or other solvent. The addition of complex formers, such as boric fluoride

or bichloride of mercury, prevents any indiscriminate diffusion of the liberated diazonium salt, better still, the diazonium salt can be converted into a completely

5 insoluble salt or double salt, for example, one of the stable preparations described in British Patent No. 372,275, and afterwards coupled with the aid of sodium acetate, sodium carbonate or alkali.

10 Residual silver bromide is converted into the more easily reacting thiourea complex by addition of some thiourea for the purpose of dissolving the antidiazotate. The thiourea complex yields the desired azo

15 dye in the presence of thiosulphate, when it is acidified even with quickly coupling neutral components. Here it is also best to convert in the presence of thiourea, first to silver antidiazotate, from which

20 the insoluble diazonium salt is formed on the image with acid and addition of the precipitants mentioned above, and then only to couple to the insoluble azo dye by bathing in a solution of the components

25 containing some excess of alkali or sodium carbonate. There can be used also the antidiazotates of dyes, and those containing an azo group, from which

30 other dyes can be formed by further image-controlled coupling in the manner described. The colour development of the silver bromide contained in the other

35 layers can be done later without difficulty. Generally, however, the component colour image is first produced in the lower red-sensitive emulsion, then the

40 silver chloride of the upper emulsion is converted through silver ferrocyanide or directly into an insoluble yellow azo dye, then the silver halide present in the

45 middle emulsion is made developable and developed. One could proceed in a similar manner when two silver chloride layers are present, of which one is situated

50 on the front side of the film, the other, yellow-green-sensitive together with the red-sensitive silver bromide emulsion, on the other side of the film. In this manner, two different azo dyes are

55 obtained, whilst the red-sensitive silver bromide layer is developed to the green-blue indophenol, or indamine.

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:—

60 1. A colour photographic element especially a film, having three differentially colour sensitive silver halide emulsion layers either all three on the same

65 side or one on one side and two on the other side of a single support, one or two of the three emulsion layers on the same side of the support, or one of the two

emulsion layers on the one side of the support, as the case may be, being silver chloride and the remainder, on that side, silver bromide.

2. A colour photographic element as claimed in claim 1 in which the middle layer consists of silver chloride emulsion and the other layers consist of silver bromide emulsion, the layers being on

70 the same or different sides of the support.

3. A colour photographic element as claimed in claim 1 in which the upper layer consists of silver chloride emulsion and the other layers of silver bromide emulsion, the middle layer being on the

80 same side of the support as the upper layer.

4. A colour photographic element as claimed in claim 1 in which the upper and lower layers consist of silver chloride emulsion and the middle layer consists of

85 silver bromide emulsion.

5. The method of colour processing a photographic element as claimed in claim 2 in which after general development the residual silver bromide in the

90 outer layers is selectively exposed and colour developed with weakly-acting colour developers and then the residual silver chloride of the middle layer in colour developed by prolonged treatment

95 with a strongly-acting colour developer.

6. A modification of the method claimed in claim 5 in which the residual silver chloride is converted into a

100 coloured salt.

7. The method of colour processing a photographic element as claimed in claim 3, which consists in developing all the latent images to silver, then

105 selectively exposing and colour developing the residual silver bromide in the lower layer, then rendering the residual silver halide in both other layers simultaneously developable and first colour

110 developing the residual silver chloride and finally colour developing the remaining residual silver bromide.

8. The method of colour processing a photographic element as claimed in claim 115 2 or 3 in which the latent image in the silver chloride layer is first selectively developed to silver and the residual silver chloride selectively colour developed

120 with a weak colour developer or converted into a coloured substance or mordanting body, and then the latent images in the silver bromide layers are developed to silver and the residual silver bromide selectively processed to colour.

9. The method of colour processing a photographic element as claimed in claim 125 2 or 3 in which the silver chloride image is converted into a coloured mercaptide.

10. The method of colour processing a 130

photographic element as claimed in claim 2 or 3 in which the silver chloride image is converted into a mordant dye image.

- 5 11. The photographic elements and methods of processing the same, substantially as herein described.

Dated this 8th day of May, 1937.

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

Abingdon : Printed for His Majesty's Stationery Office, by Burgess & Son.

[Wt. 8138.—50 /2 /1940].