[Second Edition.]

PATENT SPECIFICATION

Convention Date (Austria): May 9, 1936.

500,796

Application Date (in United Kingdom): May 10, 1937. No. 37123/38.

(Divided out of Application No. 13250/37.) (500,826).)

Complete Specification Accepted: Feb. 10, 1939.

COMPLETE SPECIFICATION.

Improvements in and relating to 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 No. 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 colour photography.

In particular it relates to improvements in processes wherein colour developed colour component records are to be produced in photographic elements having three silver halide emulsions sensitized to three separate colours covering substantially the whole of the visible spectrum.

Such an element may be a three-layer photographic element whose upper layer is not specifically colour sensitized and which contains colour sensitizers in the middle and bottom layers. The middle layer is usually yellow and green sensitive and the lower layer red sensitive. This order of the layers may be changed if a very sharp blue image is desired, by having the middle emulsion sensitive to red and orange and the lower emulsion sensitive to yellow and green. This variation has been made possible by the fact that red sensitizers which do not sensitize to green and yellow but very strongly sensitize to extreme orange red, in addition to the genuine red, for example 4:4¹-dichloro - 2:2¹:8-triethylthiacarbocyanine chloride can now be made. The three layers may be coated on the same side of the support or the red or yellow-green sensitive emulsion can be situated alone on the back of the support and the other two on the front. Alternatively, the element may have two layers on the same or different sides of the support, one layer being of the mixed emulsion type as described and claimed in application No. 34979/38.

The object of the invention is to facilitate the selective colour development of either reversed silver halide images or silver halide images obtained by reconversion of developed silver images.

According to the present invention there is provided a process of colour photography involving the selective colour development of silver salt colour component records in the three photographic silver halide emulsions on a single support in which one or two of the emulsions 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.

In specifications Nos. 440,032, 440,089 and 447,092, there are described processes for the production of coloured photographic records in elements having at least three layers on a single support by operations involving the controlled penetration of processing baths; in these specifications it is stated that whenever it is necessary, before or during the colour processing, to render the reversed or bleached images developable, this can be done by treating the element with known chemical reagents which will render the silver salt developable, for example as set forth in our prior patent No. 341,183. It is stated that such known reagents may be employed in some of the processing baths themselves.

It will be seen, however, that in the present invention the images in one or two emulsions are fogged after colour developed images have been produced in the other emulsions or a colour developed image has been produced in the remaining emulsion. The present invention is primarily concerned with processes in which the images in the three layers are individually colour developed by selectively rendering all of them developable but as will be seen, it can be employed in a process in which images in two of three superimposed layers on a single support are selectively colour developed by operations involving controlled diffusion of processing solutions.

It will be seen that the present invention enables an image to be rendered developable without the necessity for it to retain its colour sensitivity or even its

light sensitivity and the invention thereby avoids the difficulty of exposing one layer through another which may not have uniform and/or adequate transparency to the light employed.

Where the element has three differentially sensitized silver halide emulsion layers superimposed on a single support, either all on one side or one on one side and two on the other, the greatest difficulty, in a reversal process, is to make the residual silver halide of the middle layer developable without influencing the other two existing component images. The present invention enables this to be done conveniently.

Employing a three-layer element, with sensitization of the lower layer exclusively for red and orange and sensitization of the middle layer to yellow and green, the processing is, in general, as follows :

After camera or printing exposure, the superimposed latent images are first of all developed to the three black component silver images by an ordinary, non-tanning, preferably neutral developer, such as ferrous oxalate, amidol or diamido-*o*-cresol. Most other organic developers in solutions containing sodium carbonate are also suitable, since they do not noticeably harm the colour sensitivity and, if necessary, this can be at least partially restored by a known reagent such as an alkali sulphite or bisulphite.

In order to avoid the undesirable effect of local under-exposure in the lower layers it is best to saturate all three layers first in a solution of the developing agent (which does not act in the absence of alkali) of a considerably stronger concentration than usual, and then to develop in solutions of sodium carbonate, ammonia or other weak alkalies such as alkali bicarbonate, borax, trisodium phosphate or sodium aminoacetate. Alternatively a concentrated developing solution can be allowed to diffuse into all the layers at as low a temperature as it is possible to employ without alteration in composition of the solution and the development process started or accelerated by warming the layers to room temperature or above.

The residual silver halide is used for reversal development and the initially reduced silver is not removed at this stage.

EXAMPLE 1.

The element at this stage has a yellow colouring matter in the upper layer or between the upper layer and the middle layer.

The lower layer is now exposed to red light and developed blue-green. Then the upper layer is exposed to blue light and developed yellow. Since the primarily reduced silver prevents a complete exposure throughout the depth of the upper layer, some residual silver halide will be left and developed later to the colour of the middle layer. It is best, therefore, before exposure of the upper layer to treat the element briefly with a silver solvent to dissolve only the highly dispersed silver of the upper layer wholly or partially without affecting the other two layers, and then only to expose the upper layer to blue light.

The residual silver halide of the middle layer is then made developable by treating with a fogging agent and then colour developed purple. Finally all the silver is removed.

Suitable fogging agents are about a 0.02% solution of thiourea, thiosinamine or other similarly acting sulphur derivative, a 0.001% solution of stannous chloride, an arsenite, hypophosphite, thallous salt, triamido-phenol or fogging dyes, the last-named especially when used in presence of heavy metal salts. The fogging agent may be added to the colour developer.

EXAMPLE 2.

If the element has two filter layers, a yellow and a red or orange one or two yellow ones (as described and claimed in application No. 33290/38 of even date), then the lower layer can first be exposed to blue light and the further processing carried out as in Example 1. This does not require oxidation stability or even developer stability of the sensitizers.

EXAMPLE 3.

If the element has a colourless or yellow filter not transmiting ultra-violet light between the upper and middle silver halide emulsions (see application No. 34976/38 of even date) the lower layer is first exposed to red light after general development and developed in colour, then follows exposure from above with ultra-violet light and the upper layer is developed yellow; after this the middle layer is made developable with thiourea or other fogging agent and the corresponding component colour image is developed.

EXAMPLE 4.

If two ultra-violet filters are arranged on both sides of the middle silver halide layer (see application No. 34976/38 of even date) the outer layer and the lower layer are first successively exposed to ultra-violet light and colour developed and then the middle layer is made developable by treatment with thiourea or other fogging agent and colour developed. Finally all the silver is removed.

EXAMPLE 5.

If the upper layer consists of silver chloride, as described and claimed in application No. 13250/37), then advantage

can still be taken of the more ready developability of the silver chloride even when the upper and middle layers have been simultaneously made developable by treatment with fogging agents. Thus, the lower layer is exposed to red light after primary development and developed blue-green. Simultaneously in the upper and middle layers the residual silver halide is made developable with very dilute solutions of thiourea, stannous salt or other fogging agent and the same effect is obtained as through the action of light. With suitable developers, first the upper silver chloride layer, then the middle silver bromide layer are developed in colour.

EXAMPLE 6.

If the element has one layer (especially the middle layer) composed of silver chloride (as described and claimed in application No. 13250/37 of even date) and this layer is developed first, then the residual silver halide of one of the remaining layers is made developable by exposure and is colour developed and the remaining layer is made developable by treatment with a fogging agent and colour developed.

If the red-sensitive emulsion is in the middle, the procedure described in the foregoing examples can be employed with corresponding modifications.

Thus Example 5 can be modified simply by using yellow light for exposure of the lower layer. If there is a yellow colouring matter in the upper layer or between the upper layer and the middle layer as in Example 1, the upper emulsion can be made developable by exposure to blue light immediately after black development in order to obtain the yellow component image. The middle emulsion is then made devolopable by treatment with fogging agents and colour developed. Finally the bottom layer is exposed to yellow light, or after removal of all the silver, exposed to white light from both sides, for the production of the purple component image. The processes described above can be employed if two layers are on one side of the support and one on the other.

EXAMPLE 7.

If the element has two layers, one of which is of the mixed emulsion type (see application No 34979/38) and if one of the mixed emulsions consists of silver chloride as described and claimed in application No. 13250/37, and if there is present a yellow filter colouring matter in the not specifically colour sensitive layer or between that layer and the mixed emulsion layer, then, after general development, the residual silver bromide of the blue-sensitive emulsion is exposed either immediately or after removal or conversion of the reduced silver and developed yellow. The mixed emulsion layer is then made developable by treatment with a fogging agent and the silver chloride emulsion therein is then developed purple or blue-green according to its sensitivity. Finally the silver bromide of the mixed emulsion layer is developed blue-green or purple as required.

Treatment with a fogging agent to render one layer only of an element developable may also be employed in elements in which one layer is temporarily tanned, as described and claimed in application No. 24633/38 of even date. Thus, if there are three layers on one side of the support of which the lower one is tanned, the residual silver halide of the upper layer is, after general black development of the two untanned layers, exposed first to red light (or, in the presence of orange filters in the material to blue light) and developed in colour. The residual silver halide of the middle layer is then made developable by short action of a fogging agent and colour developed. Finally the lower layer after detanning, is developed black and the residual halide treated with a fogging agent and colour developed.

EXAMPLE 8.

The present invention is particularly suitable for the negative processing of a three layer element in which the middle layer is surrounded by two yellow filters or by two ultra-violet absorbing filters or by a yellow filter and an ultra-violet absorbing filter. In such a case, after simultaneous black development of all three emulsions, the residual silver halide is fixed out and then the reduced silver is reconverted into silver chloride or silver bromide. Each of the two outer emulsions is now exposed to blue or ultra-violet light (according to the nature of the filter) and developed in the proper colour. Then the middle layer is made developable by treatment with a fogging agent and colour developed. Finally, all reduced silver is removed and the filter dyes are destroyed or washed out. Such removal or destruction of the ultra-violet absorbing substance may not be required if its fluorescence is not too noticeable in the finished picture.

EXAMPLE 9.

The present invention provides an alternative method for reversal processing of the element employed in example 2. After general black development, the residual silver halide of the upper layer is exposed to blue light and colour developed by controlled penetration of a colour developer (see specification No. 454,622). The residual silver halide of the lower layer is then exposed to blue light and colour

developed. Finally the residual silver halide of the middle layer is treated with a fogging agent and colour developed.

EXAMPLE 10.

It is possible also by means of the present invention, to process conveniently a three-layer element without relying upon light filters in the element. If the sensitizer of the middle layer is resistant to development and oxidation, then after general black development the residual silver bromide of the middle layer is exposed to yellow or red light and colour developed. Then the residual silver halide of the other two layers is made developable by treatment with a fogging agent and the upper one only colour developed by controlled penetration of a colour developer (see specification No. 454,622). Finally the lower component image is colour developed.

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 process of colour photography involving the selective colour development of silver salt colour component images in three photographic silver halide 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.

2. Process as claimed in claim 1, in which the three emulsions are contained in three layers on a single support and one of the layers is treated with a fogging agent.

3. Process as claimed in claim 2, in which the middle layer is treated with a fogging agent after processing the other layers.

4. Process as claimed in claim 3, in which the upper layer is colour developed by controlled penetration of a colour developer.

5. Process as claimed in any of the preceding claims in which the residual halide of the three emulsions is treated for the production of positives by reversal.

Dated this 20th day of December, 1938.

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

Abingdon : Printed for His Majesty's Stationery Office, by Burgess & Son.
[Wt. 8253A.—11/1944.]