PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in and relating to Three-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 processes for obtaining colour photographs in elements having three silver halide emulsion layers on a single support.

It is known that the selective colour processing of reversed silver salt images in three-layers, not containing colour formers, carried on a single support, can be accomplished by controlled penetration of processing baths (see specifications Nos.:—427,518, 427,520, 454,498, 454,499 and 454,622).

The present invention is concerned with processes in which the selective processing of the silver salt images is accomplished by selectively rendering at least two of the images developable by differential exposure to light and colour developing them and then processing the third image to colour. The greatest difficulty in a process of this kind is to make the residual silver halide of the middle layer developable without influencing the other two component images. The present invention provides a means of doing this.

In particular the present invention relates to a process of producing colour developed reversed images in a photographic element of the kind having three silver halide emulsion layers in a single support of which the upper layer is not specifically colour sensitized, and of which the middle and bottom layers contain colour sensitizers (that in the lower layer at least being resistant to the action of developing agents), and having a yellow filter colouring matter which is not destroyed by development in the upper layer or between the upper layer and the middle layer.

In such three layer material the upper layer is generally blue-violet sensitive, the middle layer yellow and green sensitive, and the lower layer red sensitive. In order to limit diffusion to a minimum, it is advisable to make the two upper layers as thin as possible, about 0.005—0.0 mm., requiring the use of very fine-grain emulsion, relatively poor in silver, for three-colour reversal development.

If filter layers are interposed, strongly swelling gelatine must be used for these so that the individual layers are spaced away from one another during the chemical reactions. These filter layers are kept so thin, 0.01 and less, that no undesirable increase of light scattering ensues, despite the fact that they may swell up tenfold. The lower layer can have the normal thickness of 0.02 mm. or for reversal development, 0.01—0.015 mm., so that the total thickness of the three layers is about 0.025—0.04 mm. While the two upper layers require developers which deposit intensively dye the image, less intensity is required for the lower layer, since this layer may contain considerable more silver halide than the upper and middle layers.

In order to obtain a vigorous, well-graded blue image, which is of primary importance for the character of the colour photograph, coating of the lower red-sensitive emulsion (or infra-red sensitive for printing elements) of an average thickness of about 0.02 mm. using a highly sensitive emulsion of medium soft gradation, preferably sensitized only for red and orange, is recommended. Above this, the yellow and green-sensitive emulsion of medium sensitivity and a thickness of not more than 0.01 mm. is coated, and over that a not specially colour sensitized emulsion also of medium sensitivity and a thickness of 0.005—0.01 mm. For this purpose, a transparent, coarse-grain silver bromide emulsion can be used. Finest grain emulsions, are however, to be preferred,

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because their blue and blue-green sensitivity can be strongly increased by modern sensitizers (see, for example, British Patent No. 376,746).

The order of the three layers just described can be changed, if a very sharp blue image is desired, by having the upper emulsion sensitive to blue-violet, the middle emulsion to red and orange or infra red and the lower emulsion to yellow and green: in which case they are developed lemon-yellow, green-blue and purple respectively. It is less desirable to arrange the layers so that the upper emulsion is red sensitive, the middle emulsion yellow-green sensitive and the lower emulsion blue sensitive, because although there are red sensitizers produced today, which in stronger concentration sensitize better for red than for blue, and this effect can still be increased by adding desensitizers for blue, nevertheless, there is, as a rule, an unavoidable greater increase in general sensitivity.

These variations have been made possible by the fact that red sensitizers which do not sensitive to green and yellow but very strongly sensitize to the extreme orange red, in addition to the genuine red, for example 4:4¹-dichloro-2:2¹:8-triethyl-thiacarbocyanine chloride, can now be made.

The insertion of a yellow filter layer, transmitting also red rays, between the blue-sensitive and the middle yellow-green or red-orange-sensitive emulsion layers is generally necessary for exposure purposes, even if the blue rays are generally absorbed by a yellow filter layer, because there are no means at present permitting complete suppression of the blue-sensitivity of the two other emulsions. A green filter between the middle and lower layers is generally unnecessary for exposure purposes and a red-orange filter is very seldom required since many of the present-day orange-red sensitizers are without effect in the green and yellow parts of the spectrum.

If the filter dyes necessary for the division of the spectrum into three parts are added to the silver halide emulsion layers; namely, yellow to the blue-sensitive layer, red-orange or green to the middle layer, the true colour is to a certain degree affected, because, regardless of the thinness of the layers, formation of the latent image can take place only in the upper part of each emulsion layer; this effect is most noticeable in reversal development.

The use of intermediate layers as colour filters is strongly recommended, because strongly swelling gelatine layers between the silver halide emulsions appear necessary for reasons of development-technique. It is usually sufficient to colour the gelatine layer adjacent to the blue-sensitive emulsion yellow, or also the blue-sensitive emulsion itself. The other intermediate layer, if it is present at all, may remain colourless, or may also be coloured yellow instead of red or green. The whole triple layer with one or more intermediate layers, or without them, may also be coloured yellow throughout; most simply by subsequent bathing in dye solutions.

As will be seen, the filter colouring matters which are present in the element treated according to the present invention serve not merely to protect the emulsions against the action of undesired light during camera exposure, but the yellow colouring matter in the upper layer or between the upper layer and the middle layer serves to facilitate subsequent processing. Accordingly it must be resistant at least to the first developer.

The three emulsion layers may be coated on the same side of the support or the red or yellow-green sensitive emulsion, that is, the lowest layer, can be situated alone on the back of the support and the two others on the front.

In the process of the present invention, it is assumed that both the colour sensitizers are stable at least to a neutral black developer and to the first weakly alkaline colour developer. This is true of most known sensitizers. An advantage of the present invention is that the sensitizers in the middle and lower layers need not be stable to oxidation. According to the present invention there is provided a process of producing colour developed reversed images in a three-layer photographic element of the kind hereinbefore defined, which consists in developing the first latent images to silver, then exposing the residual silver salt image in the lowest layer only by coloured light to which the other layers are not sensitive, then colour developing the exposed residual silver salt image in the lowest layer, then exposing the residual silver salt in the upper layer by blue light and colour developing the exposed residual silver salt image in the upper layer, then colouring the reversed image in the middle layer and finally removing the positive and negative silver from all the layers.

With sensitization of the lower layer exclusively for red or for red and orange, and sensitization of the middle layer to yellow and green, the process 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.

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 through the depth of the upper layer, some residual silver halide will be left and developed later in the colour of the middle layer. It is better, therefore, to treat the upper layer before exposing it to blue light briefly with a silver solvent dissolving only the silver of the upper layer without allowing it to act on the other two layers. Only then is the upper layer exposed to blue light and developed yellow. Then the middle purple component image is obtained by one of the following methods.

A. The middle layer is treated with a colour developer which acts so vigorously on addition of ammonia or caustic alkali or of alcohol or acetone, preferably out of contact with air, that the residual silver halide is reduced without exposure, by prolonged treatment. This method is particularly suitable if the upper layer consists of silver chloride, as described and claimed in application No. 13250/37, since silver chloride is quite stable, when unexposed, to the colour developers containing sodium carbonate required for the other layers. Even if the residual silver halide of the middle layer is silver bromide, this is reduced without pre-treatment or exposure by most leuco vat dyes in alkaline solution or in a solution containing alcohol or acetone (as described and claimed in application No. 35101/38 of even date) and the dye can be precipitated on the image (as described and claimed in application No. 24632/38 of even date).

Residues of the latent images in the other two layers can be previously destroyed by the action of mild oxidizing agents such as a mixture of potassium ferricyanide and ammonia.

B. The residual silver halide of the middle layer is made developable by exposure from above or from both sides to ultra-violet light or, better still, to soft X-rays and the appropriate component image is colour developed. This is possible because very fine grain and non-coherent reduced silver is very transparent to ultra-violet light.

C. The residual silver bromide of the middle layer is converted into silver iodide or one of its complex salts and this is coloured purple by mordanting dyes, which may be made insoluble as described and claimed in application No. 35100/38 of even date.

The metallic silver is now removed from all the layers.

If the red sensitive emulsion is in the middle, then the above described procedure is correspondingly changed, e.g. the bottom layer is exposed to green light and developed purple after the primary development and the middle layer is coloured blue-green.

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 producing colour developed reversed images in a three-layer photographic element of the kind hereinbefore defined, which consists in developing the first latent images to silver, then exposing the residual silver salt image in the lowest layer only by coloured light to which the other layers are not sensitive then colour developing the exposed residual silver salt image in the lowest layer, then exposing the residual silver salt in the upper layer by blue light and colour developing the exposed residual silver salt image in the upper layer, then colouring the reversed image in the middle layer and finally removing the positive and negative silver from all the layers.

2. Process as claimed in claim 1, in

which the reversed image in the middle layer is colour developed without exposure by prolonged action of a colour developer containing ammonia or caustic alkali or alcohol or acetone.

3. Process as claimed in claim 1, in which the residual silver halide of the middle layer is made developable by exposure from above or from both sides to soft X-rays and developed.

4. Process as claimed in any of the preceding claims which for the first development, all the layers are impregnated with the developing agent in high concentration and are then treated with weak alkali to effect development.

5. Process as claimed in any of the preceding claims, in which for the first development all the layers are impregnated at a low temperature with concentrated developing solution and are then heated to effect development.

Dated this 17th day of December, 1938.

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Chartered Patent Agents.

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