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COMPLETE SPECIFICATION

Improvements in Colour Photographic Elements

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 Czechoslovakia), 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 photographic elements.

In particular the invention relates to sensitive photographic elements having three 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 the extreme orange red, in addition to the genuine red, 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 of which contains two sets of silver halide grains respectively sensitized for the red and green regions of the spectrum while the other consists of not specially sensitized silver halide.

The object of the present invention is to facilitate the selective re-exposure of either reversed silver halide images or silver salt images obtained by reconversion of silver images. This is done by giving one of the emulsions a sensitivity to light outside the region it is destined to record and to which it is sensitized, such as to infra-red light, by means of another sensitizer which is stable to developing or developing and oxidising baths. It then becomes possible to employ for the re-exposure of that emulsion (i.e. exposure of the reversed or reconverted images) the appropriate light to which the silver salt is sensitive, e.g. infra-red light, so that the other emulsions are unaffected thereby. Thus, an infra-red sensitizer, such as cryptocyanine or neocyanine, stable to the correspondingly selected developer, can also be added to one of the colour-sensitized layers, usually to the lowered sensitive layer, which by second exposure of the residual silver bromide with infra-red, permits the individual colour development of this layer alone. Infra red, under normal conditions, seldom plays any part in the camera exposure.

The emulsions can also be coated on the support in reverse order, if the exposure is made through the back.

In a three-layer element, for example, the lowest layer may contain a colour sensitizer, which is resistant to development and the middle layer an infra-red sensitizer, which is resistant to develop- (in addition to the colour sensitizer of the middle layer).

In specification No. 427,519 there is described and claimed a multi-layer photographic sensitized film in which the layers are substantially uncoloured, but differentially colour sensitized, and in which one of the said layers is sensitized to infra-red. Preferably, the infra-red sensitized layer is the silver layer on one side of the support. In the film disclosed in detail in that specification, the infra-red sensitized layer was not colour sensitized, and its purpose was to facilitate the recording of an image by means of light to which the other two layers were insensitive. As will be seen, the elements according to the present invention are distinguished from the film described in this prior specification by the fact that one of the emulsions which is

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sensitized to colour also contains an additional sensitizer which may be an infra-red sensitizer.

For three-colour reversal development, the procedure is, in general, as follows:—

After camera or printing exposure, the super-imposed 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 is practicable and the development process started or accelerated by warming the layers to room temperature or above.

The residual silver halide may be used for reversal development or this may be converted in one or more layers to silver chloride in a fine state of subdivision, by treatment with potassium ferricyanide and sodium chloride or with lead chloride or with mercuric chloride. The removal of the initially reduced silver may be effected by completely dissolving it with oxidizing agents and washing it out.

After general black development the lower layer is exposed to red light and developed blue-green, (assuming it is sensitized to red, and the middle layer is then exposed through the uniformly blackened lower layer to infra-red light. This latter requires long exposure. The upper layer can then be exposed to blue or ultra-violet light or to soft X-rays and colour developed and the silver finally removed from all of the layers.

Alternatively, if two ultra-violet filter layers are arranged on both sides of the middle layer, this middle layer may contain an infra-red sensitizer so that after the outer layers have been exposed to ultra-violet light and colour developed, the middle layer may be exposed to infra-red light and colour developed.

If the middle layer of a three-layer element is composed of silver chloride, this may also contain an infra-red sensitizer, then the middle layer alone may first be developed black with a weak ordinary developer and the residual silver chloride exposed to infra-red light and colour developed. Only then are the latent images in the outer layers developed and the residual silver halide therein successively exposed and colour developed, taking advantage of the developed silver in the middle layer to act as a light screen permitting individual exposure of the outer layers.

In a three-layer element in which the upper or middle emulsion consists of silver chloride, this emulsion or the bottom emulsion may contain an infra-red sensitizer which is stable to the developer and to mild oxidizing agents. The residual silver halide of such emulsion can then be made developable through infra-red light, even if the original sensitizer has become ineffective. Any other sensitizer could, however, be added to the lower emulsions in addition to that for red (or green as the case may be) for which the middle emulsion is insensitive.

An infra-red sensitizer, which is stable to the developer, can generally be added to the lower emulsion in addition to the red sensitizer. After general primary development, the residual silver bromide of this emulsion is first exposed to infra-red rays and developed in colour, the other two emulsions can then be made developable with thiourea, or other fogging agent and first the silver chloride, then the silver bromide emulsion developed in colour.

In a two-layer element in which one layer contains two sets of silver halide grains respectively sensitized for the red and green regions of the spectrum while the other consists of not specially sensitized silver halide, the latter layer may consist of a silver chloride emulsion and the mixed grain-layer may consist of red-sensitized and green-sensitized grains of which the red-sensitive grains may contain in addition an infra-red sensitizer whose sensitizing ability survives the general black development, or can be easily regenerated. After general black development, the mixed grain layer is exposed to infra-red light and the exposed part of the residual grains developed blue-green. All residual silver halide is made developable by thiourea, or other fogging agent and the silver chloride alone developed yellow, then the silver bromide of the other type of grains is developed purple, and finally all silver removed. If the blue-sensitive emulsion consists also of silver bromide, it is recommended to choose a sensitizer for the green-sensitive

grains which survives the development, and to develop the residual silver bromide of this layer purple after exposure to yellow-green light; the yellow image is then developed in the blue-sensitive emulsion which has been exposed to ultra-violet light. If the blue-sensitive silver bromide emulsion is on the other side of the film, this and the type of grains sensitized to yellow-green can be made developable simultaneously by thiourea or other fogging agent, after formation of the blue-green image, and each side developed in different colours.

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 sensitive photographic element having three silver halide emulsions respectively sensitized to three separate colours covering substantially the whole of the visible spectrum in which one of the emulsions is sensitized to yellow-green or to orange-red by means of a sensitizer and is also sensitized to another region by means of another sensitizer which is resistant to developing or developing and oxidising baths.

2. A sensitive photographic element having three silver halide emulsions respectively sensitized to three separate colours covering substantially the whole of the visible spectrum in which one of the colour sensitized emulsions also contains an infra-red sensitizer which is resistant to development.

3. A sensitive photographic element having three silver halide emulsion layers inseparably coated on a single support which emulsion layers are respectively sensitized to three separate colours covering substantially the whole of the visible spectrum in which one of the colour sensitized emulsion layers also contains an infra-red sensitizer which is resistant to development.

4. A sensitive photographic element as claimed in claim 3 in which the middle layer contains the infra-red sensitizer.

5. A sensitive photographic element as claimed in claim 2, 3 or 4, in which the infra-red sensitizer is stable to development and mild oxidizing agents.

Dated this 30th day of November, 1938.
W. P. THOMPSON & CO.,
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Chartered Patent Agents.

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