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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 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 processes of colour photography and, in particular, multi-layer colour photography.

In particular the invention relates to the colour processing of a multi-layer colour photographic element having three gelatine-silver halide emulsions on a single support of which one is not specifically colour sensitized while the other two are sensitized to red and green respectively. The objects of the invention is to facilitate the individual processing of the respective emulsions by development. In many cases it is not necessary to rely, for example, on persistence of the colour sensitivity of silver halide images remaining after reversal.

This object is secured, according to the invention, by providing and employing a multi-layer colour photographic element having three gelatino-silver halide emulsions in two or three layers on a single support one of which is not specifically colour sensitized while the other two are sensitized to the red and green or yellow-green portions of the spectrum respectively, in which one or two of the silver halide emulsion layers is or are rendered less accessible to developing solutions than the other silver halide emulsion layer or layers by temporary hardening of the gelatine in order to facilitate differential colour processing.

The invention also includes a modification of such multi-layer colour photographic element in which one or more of the silver halide emulsion layers is or are rendered less accessible to developing solutions than the other silver halide emulsion layer or layers by being formed of collodion silver halide emulsion in order to facilitate differential processing. Thus in an element having three silver halide emulsion layers coated on the same side of a single support, the lowest emulsion layer may suitably be a temporarily hardened gelatine or a collodion silver halide emulsion. In an element having one silver halide emulsion layer coated on one side and two silver halide emulsion layers coated on the other side of a support, the lower of the two emulsion layers may be a temporarily hardened or a collodion silver halide emulsion.

The invention also includes the method of processing a multi-layer photographic element as defined above in which colour component images in the more accessible silver halide emulsion layers are colour developed without affecting the image or images in the hardened gelatine or collodion silver halide emulsion layer or layers and thereafter the image or images in the hardened gelatine or collodion emulsion layer or layers is or are colour developed.

The present invention may be used to facilitate the individual primary development or reversal development of the images in the layers of a three layer colour photographic element as well as in a two-layer colour photographic element of the kind in which one emulsion layer contains two sets of silver halide grains respectively sensitized for the red and green or yellow-green regions of the spectrum and a second emulsion layer contains not specially sensitized silver halide, especially such an element in which silver chloride is used for one kind of grain or for the front emulsion or where the silver halide emulsions are arranged on different sides of the support. One advantage of the present invention is that the use of sensitizers which are stable to developing agents and oxidising agents is not absolutely essential.

Thus, in an element having three

[*Price* 1/-]

gelatino-silver halide emulsion layers of which one of the outer layers is not specifically colour sensitized and the other layers are respectively sensitized to the red and green portions of the spectrum, one or both lower layers may be tanned. One may in addition take advantage of the easy developing ability or reducability of silver chloride in comparison with silver bromide by employing silver chloride either in an untanned or in a tanned layer. Alternatively one may take advantage of the easy reducability of highly dispersed silver bromide as compared with coarse-grain silver bromide by employing the former either in an untanned or in a tanned layer.

If diffusion of the reaction solutions into the layers is controlled by the use of loading agents (See specifications Nos. 427,518, 427,520, 454,498, 454,499 and 454,622) better results are obtained if one or more lower silver halide emulsion layers are temporarily hardened according to the present invention. The individual colour development is most easily successful in all cases, if the component emulsions are arranged with one or more on one side and one or more on the other side of the support. The individual processing of the emulsion layers can be facilitated by making use of the remaining colour sensitivity of the residual silver halide, in the case of reversal development.

In processing such a three-layer element by reversal, stability of the sensitizers to oxidizing agents is, however, unnecessary, if a silver halide emulsion, usually that which is adjacent to the support, is tanned. This stability is necesasry only to development, and this condition is fulfilled by almost all sensitizers. The middle emulsion is generally yellow-green-sensitive, and the lower only red-sensitive; the sensitizer for the top or middle emulsion must be stable to the developer, but need not be stable to oxidation. The reversal processing can then be as follows:

1. If advantage is taken of stability of the sensitizer of the middle layer to the developer, both upper layers are developed black in the usual manner, the middle layer exposed to yellow light through the back and developed in colour, then the upper silver halide layer (which is coloured yellow or separated from the middle layer by an intermediate yellow filter layer) exposed to blue light and then also developed in colour. Finally, the lower layer is detanned or immediately developed black by prolonged action of a vigorous developer; then its residual silver halide is exposed and developed in colour, and the silver removed.

2. If advantage is taken of the stability of the sensitizer in the upper layer to the developer and if the lower tanned emulsion alone contains silver chloride or highly dispersed silver bromide (the other layers consisting of ordinary silver bromide emulsions), then, after general black development of the two other layers, the residual silver bromide of the upper layer is exposed first to red light, (or, in the presence of orange filters in the material, to blue light) and developed in colour; that of the middle layer is then made developable by short action of thiourea, stannous salt or other chemical fogging agent, and converted into the corresponding component colour image. Then, after preliminary detanning, follows black development of the lower silver halide emulsion and colour development after exposure through the back, or similar pre-treat ment of the residual silver halide with thiourea, or other chemical fogging agent. After completion of the two upper component colour images, the first development of the lower tanned emulsion can be omitted here and in similar cases, if some thiourea is added to the colour developer which results, as is known, in reversal with formation of the correctly coloured image; this method is, however, somewhat uncertain.

In processing a three-layer element by primary development, i.e. to produce a coloured negative from the latent images, one can also use an element having only one tanned silver halide emulsion layer. This will usually be the red-sensitive silver bromide gelatine layer adjacent to the support, which is so strongly tanned that it is not developed in the general black development, nor in the individual colour development of the two other layers, but only after destroying the tanning. The upper layer consists of silver chloride or highly dispersed silver bromide, the middle layer of fine-grain or also coarse-grain silver bromide sensitized for green-yellow; strongly swelling gelatine is used for both. The silver chloride or highly dispersed silver bromide emulsion is developed first, then the middle silver bromide layer is developed in a more vigorous developer to the corresponding component colour image, or these two layers are fixed alone, since thio-sulphate cannot penetrate the lower tanned emulsion in the moderate time required for fixing the upper layers. The last component image is now developed with a stronger alkaline colour developer, after preliminary detanning. One proceeds similarly, if the order of the layers

is reversed. The emulsion adjacent to the support is blue-sensitive and tanned, above it is the middle green-yellow sensitive layer, and on top the red-sensitive emulsion.

Instead of a tanned lower silver halide emulsion, one can also use silver bromide collodion emulsion with general or colour sensitivity increased by sensitization. After colour development of the two upper emulsion layers, the collodion is made permeable by alcohol and developed in colour.

Both lower silver halide emulsions can also be tanned. In this case, however, a silver chloride emulsion has to be used for the lower layer and the element, therefore, is most suitable for exposure through the back. The upper red-sensitive silver halide emulsion is untanned and is first developed in colour. After detanning, the lower silver chloride emulsion and then the middle emulsion are developed in colour. The element is less practical for exposure from the front, because silver chloride would then have to be used for the middle green-sensitive emulsion, and this would require very high-aperture objectives on account of the lower light sensitivity. The upper blue-sensitive silver bromide gelatine emulsion is first developed in colour, then the middle silver chloride emulsion, and finally the lower silver bromide emulsion, followed by removal of all silver and fixing.

A very fine-grain silver chloride gelatine emulsion or collodion emulsion can first be coated on the film, the amount of silver contained therein being very small and above it a silver bromide gelatine emulsion sensitized for green-yellow. Both these or the middle silver halide emulsion layer are fairly well hardened by formalin or better still, by the more recent tanning agents such as glyoxal or its derivatives. One can also coat an emulsion of silver chloride collodion sensitized in the same manner, and above this a tanned silver bromide gelatine emulsion; or both lower layers may consist of collodion. The upper layer then consists of a soft red-sensitive silver bromide gelatine emulsion. The silver chloride emulsion can also be arranged in the middle. The normally compounded green-blue developer will only develop the untanned red-sensitive emulsion during the usual time of action. By using a colour developer which is so weakly acting that it will develop only silver chloride and not silver bromide and by prolonging its action so that it can penetrate the tanned silver halide emulsion layer the corresponding component image is obtained, and the corresponding component colour image is next developed from the silver bromide of the lower emulsion with a vigorous, perhaps ammoniacal colour developer, or one containing fixed alkali; the silver is finally removed with Farmer's reducer.

Tanning of the emulsion can be entirely or partially destroyed, i.e. detanning can be effected, by alkalies, oxalates, etc., and suitable substances may be added for this purpose to the colour developer itself. The procedure is analogous in three-colour reversal development of similar three-layer elements.

One may also use a three-layer element in which the lower layer is a coarse-grain and tanned silver bromide emulsion, the middle layer is a coarse-grain silver bromide emulsion and the upper layer is a fine-grain silver-bromide emulsion. In direct or reversal colour development, the highly dispersed silver bromide latent or residual image is first colour developed, then that in the middle layer and finally that in the lower layer. The silver is then removed.

The three silver halide emulsion layers may be distributed between the two sides of the support as follows:

On the two layer side of the film, a middle hardened silver bromide gelatine or collodion emulsion may be coated, and above it a non-hardened gelatine emulsion containing highly dispersed silver bromide. The upper and lower layers (i.e. the single layer on one side and the upper layer on the two layer side) are individually developed, most of the silver halide is fixed out and the middle tanned layer is developed into the corresponding colour, after detanning, and finally the silver is removed. Such a three layer element could, of course, also be used for three-colour reversal development.

The silver halide emulsion situated alone on one side of the film can also consist of a red-sensitive collodion emulsion. If the middle silver halide emulsion layer on the other side consists of the same emulsion, the thickness of the cellulose acetate film, or other transparent support, and with it refraction, can be considerably reduced.

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 multi-layer colour photographic element having three gelatino-silver halide emulsions in two or three layers on a single support one of which is not specifically colour sensitized while the other two are sensitized to the red and

green or yellow-green portions of the spectrum respectively, in which one or two of the silver halide emulsion layers is or are rendered less accessible to developing solutions than the other silver halide emulsion layer or layers by temporary hardening of the gelatine in order to facilitate differential colour processing.

2. A modification of the multi-layer colour photographic element claimed in claim 1 in which one or two of the silver halide emulsion layers is or are rendered less accessible to developing solutions than the other silver halide emulsion layer or layers by being formed of collodion emulsion in order to facilitate differential processing.

3. A multi-layer photographic element as claimed in claim 1 or 2 in which the element has three silver halide emulsion layers coated on the same side of a single support of which the lowest is a temporarily hardened gelatine emulsion or a collodion emulsion, respectively.

4. A multi-layer photographic element as claimed in claim 1 or 2 in which the element has one silver halide emulsion layer coated on one side and two emulsion layers coated on the other side of a support of which two emulsion layers the lower is a temporarily hardened gelatine emulsion or a collodion emulsion, respectively.

5. The method of processing a multi-layer photographic element as claimed in any of the preceding claims in which colour component images in the more accessible silver halide emulsion layers are colour developed without affecting the image or images in the hardened gelatine or collodion emulsion layer or layers and thereafter the image or images in the hardened gelatine or collodion emulsion layer or layers is or are colour developed.

6. The method as claimed in claim 5 in which colour development of an image in a gelatine layer hardened by tanning is effected after detanning.

7. The method as claimed in claim 5 in which the collodion emulsion layer is made permeable by alcohol and the image therein colour developed.

8. The method as claimed in any of claims 5 to 7 in which the element is processed by reversal.

Dated this 20th day of August, 1938.

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