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 Uhlandstrasse 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 specification:

This invention relates to processes of colour photography and in particular to the colour processing of multi-layer three-colour photographic elements.

It is known that the selective colour processing of reversed silver halide 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.)

In particular it relates to a process of producing colour developed reversed images in a three-layer photographic element whose upper layer is not specially 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. The 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 the extreme orange red in addition to the genuine red, for example 4:4'-dichloro-2:2'-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 two others on the front.

In the elements which are employed in the present invention, the sensitizers in the middle and lower layers are stable to photographic developing baths and to mild silver-oxidising baths and this makes it possible to render the reversed silver halide images selectively developable merely by exposure to light of the colour to which the emulsions are respectively sensitive without requiring the presence of colour filters in the element which are stable to such processing baths. In order to avoid the difficulty that the lower two emulsions are sensitive to the blue light which is used for exposing the upper emulsion, such exposure of the upper emulsion is done last.

According to the present invention there is provided a process wherein the first latent images in the three-layer element are developed to silver and the silver removed and the reversed images are selectively processed to colour, which is characterised by the fact that the three-layer element contains colour sensitizers which are stable to photographic developing baths and to mild silver-oxidising baths and by the fact that either (a) the reversed silver halide image in the middle layer is first selectively made developable by exposure to coloured light and developed to colour; or (b) the reversed silver halide image in the bottom layer is selectively made developable by exposure to coloured light from the back and developed to colour and finally the reversed silver halide image in the top layer is made developable by exposure to light and developed to colour; or (c) the reversed silver halide image in the bottom layer is first selectively made developable by exposure to coloured light and developed to colour, then the reversed silver halide image in the middle layer is made developable by exposure to light and developed to colour. In either case it will be seen that the not specially sensitized layer is exposed and developed to colour last.
Suitable known sensitizers are: (a) For red, 2,2'-dimethyl-8-ethyl-3:4:3':4'-dibenzthiazocarboyanine iodide; (b) For yellow-green, 2,1'-diethyl-9:4-benzthia-
2'-cyanine iodide.

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, amido 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 develop in solutions of sodium carbonate, ammonia or other weak alkalis 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 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, as described and claimed in co-pending application No. 26472/38 (Serial No. 501,008). The removal of the initially reduced silver may be effected by completely dissolving it with oxidizing agents and washing it out. It is sufficient if at least the silver of the upper layer and all or a part of the silver of the middle layer is removed in this manner when the reversed silver halide image of the middle layer is to be exposed from above. For the colour processing, the residual silver halide of the middle layer is exposed to yellow or green light from either side and developed purple. After this, the silver halide of the lower layer is exposed to red light through the back and developed green-blue. Finally, the residual silver halide of the upper layer is exposed to blue or ultra-violet light and developed yellow. A variant of this procedure is to expose the lower layer first to red light and develop green-blue, then expose the middle layer to yellow light from above, and develop purple, and finally expose and develop the top layer as before. In the above description it is assumed that the sensitizers of the middle and lower layers are stable to mild silver-oxidizing baths. This condition can be secured most easily if the silver to be acted upon is highly dispersed silver, since in this condition it requires less drastic treatment. Such condition results from the use of very fine-grain silver halide emulsions for the upper and middle layers at least. Such emulsions, however, require an extremely fast lens for exposure unless the element is used for printing purposes from colour negatives or black separation images. The colour sensitivity can, however, be partially restored by dilute solutions of alkali sulphite, alkali bisulphite or of hydrazine sulphate.

If the red sensitive emulsion is in the middle, then the above described procedure is correspondingly changed, e.g., the middle layer is exposed to red light after removal of the primarily reduced silver and developed blue green, the lower emulsion is next exposed to yellow light and colour developed and finally the upper emulsion is exposed to blue light and 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 three-layer colour photographic process wherein the first latent images are developed to silver and the silver removed and the reversed images are selectively processed to colour, which is characterised by the fact that the element contains colour sensitizers which are stable to photographic developing baths and to mild silver-oxidizing baths and by the fact that the reversed silver halide image in the middle layer is first selectively made developable by exposure to coloured light and developed to colour, then the reversed silver halide image in the bottom layer is selectively made developable by exposure to coloured light from the back and developed to colour and finally the reversed silver halide image in the top layer is made developable by exposure to light and developed to colour.

2. A three-layer colour photographic process wherein the first latent images are developed to silver and the silver removed and the reversed images are selectively developed to colour.
processed to colour, which is characterised by the fact that the element contains colour sensitisers which are stable to photographic developing baths and to mild silver-oxidizing baths and by the fact that the reversed silver halide image in the bottom layer is first selectively made developable by exposure to coloured light and developed to colour and then the reversed silver halide image in the middle layer is made developable by exposure to coloured light from the front and developed to colour and finally the reversed silver halide image in the top layer is made developable by exposure to light and developed to colour.

3. Process as claimed in claim 1 or 2 in 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.

4. Process as claimed in claim 1 or 2, in which for the first development all the layers are impregnated at a low temperature, as herein described, with concentrated developing solution and are then heated to effect development.

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