

## PATENT SPECIFICATION

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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 Otten-  
dorfergasse 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:—

The present invention relates to processes  
of and materials for obtaining colour  
photographs by multiple colour develop-  
ment and in particular to elements having  
three differentially colour sensitized silver  
halide emulsions on a single support and  
the processing thereof.

The invention may be applied to a three  
layer material, i.e. one in which three  
differentially colour sensitized silver halide  
emulsion layers are coated on a single  
support, or to a two layer material of the  
kind in which one layer contains a mixture  
of silver halide emulsions respectively  
sensitized for the red and green regions  
of the spectrum and a second emulsion  
layer consisting of a not specially colour  
sensitized silver halide emulsion.

In the 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—0.01 mm,  
requiring the use of very fine-grain emul-  
sions, 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 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 thick-  
ness 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 emul-  
sion 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 pre-  
ferred, 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 re-  
spectively. 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.

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These variations have been made possible by the fact that red sensitizers which do not sensitize to green and yellow or very strongly sensitize the extreme orange red, in addition to the genuine red, for example 4 : 4<sup>1</sup>-dichloro-2 : 2<sup>1</sup> : 8-triethyl-thiacarbocyanine chloride, can now be made.

The insertion of a yellow filter, 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 red-orange sensitizers are without effect in the green and yellow parts of the spectrum.

Filter layers may, however, be required to facilitate selective re-exposure of the layers in the colour processing, for example as described in co-pending applications Nos. 33290/38, 26471/38, 26470/38 and 34976/38.

The middle silver halide layer may also be surrounded by filter layers absorbing ultra-violet and containing colourless or correctly coloured filter-substances absorbing ultra-violet, if desired, in addition to the usual filter dye. Since a yellow filter layer under, or yellow colouring of the blue-sensitive emulsion is employed for purposes of exposure, a filter layer absorbing ultra-violet alone can only be interposed between the middle and lower layer. This feature forms the subject of application No. 34976/38 of even date.

The present invention is concerned with a method for preventing or restricting the diffusion of such filter colouring matters.

According to the present invention, a photographic element has three differentially sensitive silver halide emulsions on a single support and a filter colouring matter or matters in an intermediate layer or intermediate layers between two emulsion layers, which filter colouring matter is precipitated *in situ* to render it resistant to diffusion. The three emulsions may be coated one over another on the same side of the support. The method of the invention consists in introducing a water-soluble colouring matter into gelatine which is to constitute the intermediate layer and precipitating it therein.

Basic filter dyes can be precipitated by high molecular weight sulphonic acids, as diazo light yellow 2 G (Rowe's Colour Index No. 654), di (*p*-aminobenzoyl)- $\alpha$ -naphthyl-

amine sulphonic acid, anthraquinone sulphonic acid etcetera, but best by complex inorganic acids, such as, phosphotungstic acid, silicotungstic acid, phosphomolybdic acid, or their salts, as well as their easily prepared reduction products.

Suitable colouring matters for the filter layers are described in application No. 33290/38 of even date.

The present invention is particularly suitable for use in connection with a three-layer element which is to be processed to colour by reversal. Such an element may be as described in co-pending application No. 26469/38 but having, in addition, in the upper layer or in a gelatine layer between the upper emulsion layer and the middle emulsion layer a yellow dyestuff which has been precipitated *in situ* to render it resistant to diffusion and which is not destroyed by the action of developing agents and mild oxidizing agents.

The method of reversal colour processing of such an element then consists in first developing the latent images to silver, removing the silver, selectively exposing and colour developing the upper and lower layers in either order, removing the newly reduced silver in the upper layer and then exposing the middle layer and colour processing it. The development of the latent images to silver and the removal of the reduced silver may be accomplished by the methods described in the aforesaid co-pending application. The residual silver halide may be used for reversal or it may be converted into finely divided silver chloride as described and claimed in co-pending application No. 26472/38.

If the lower layer is sensitized to red light then this lower layer is then first exposed to red light and developed blue-green, then the upper layer to blue light and developed yellow. The order of these steps may be reversed. The newly reduced highly dispersed silver of the upper layer is then removed by means of a silver solvent and the middle layer made developable with yellow light and developed purple. If the red sensitive emulsion is in the middle, the processing is correspondingly changed.

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 photographic element having three differentially colour sensitized silver halide emulsions on a single support and a filter colouring matter or matters in an intermediate layer or intermediate layers between two emulsion layers, which filter colouring matter is precipitated *in situ* to render it resistant to diffusion.

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2. A photographic element as claimed in claim 1 in which the three emulsions are coated in layers one over another on the same side of the support.
- 5 3. A photographic element as claimed in claim 1 in which the three emulsions are coated in layers one over another so that the blue sensitive layer is uppermost and a gelatine layer between the blue sensitive  
10 layer and the other layers contains a yellow colouring matter which has been precipitated therein.
4. A method of preparing a photographic element as claimed in any of the  
15 preceding claims in which a water soluble colouring matter is introduced into gelatine which is to constitute the intermediate layer and is precipitated therein.
5. A method as claimed in claim 4 in  
20 which the precipitant is a complex inorganic acid.
6. A photographic element having three silver halide emulsion layers of which the upper one is sensitive to blue and the lower two are sensitized to red and green  
25 respectively, in which there is present in a gelatine layer between the upper emulsion layer and the middle emulsion layer a yellow dyestuff which has been precipitated  
30 *in situ* to render it resistant to diffusion.
7. The method of reversal colour processing of the element claimed in claim 6, and in which the sensitizers in the layers and the yellow dyestuff are not destroyed  
35 by the action of developing agents and mild oxidising agents which consists in first developing the latent images to silver, removing the silver, selectively exposing and  
40 colour developing the upper and lower layers in either order, removing the newly reduced silver in the upper layer and then exposing the middle layer and colour  
developing it.

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