Improvevements 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 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 statements:

This invention relates to processes for obtaining colour photographs in elements containing 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, 427,620, 424,493, 424,499 and 424,623). 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 coloring 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 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 100 emulsion can be used. Finest grain emulsions, are however, to be preferred,
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′:4′-dichloro-2′:2′-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 thickness 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-tan-
ning, preferably neutral developer, such as ferrous oxalate, amidol or diammoni-
cresol. Most other organic developers in solutions containing sodium carbonate are
also suitable, since they do not noticeably harm the colour sensitivity and, if neces-
sary, this can be at least partially
10 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
15 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 concen-
tration than usual, and then to develop in solutions of sodium carbonate,
ammonia or other weak alkalis such as
20 alkali bicarbonate, tri-sodium phosphate or sodium amoniacocetate. Alter-
natively a concentrated developing solution
can be allowed to diffuse into all the
25 layers at as low a temperature as is 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 tempera-
30 ture or above.

The residual silver halide is used for
reversal development and the initially
35 reduced silver is not removed at this
stage.

The lower layer is now exposed to red
light and developed blue-green. Then the up-
40 per 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
45 it to blue light briefly with a silver
sensitizing solution 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
50 purple component image is obtained by
one of the following methods.

A. The middle layer is treated with a
55 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
60 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 con-
65 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
70 and claimed in application No. 35101/38
of even date) and the dye can be precipi-
tated on the image (as described and
claimed in application No. 24632/38 of
75 even date).

Residues of the latent images in the
other two layers can be previously
90 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
85 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
95 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
100 all the layers.

If the red sensitive emulsion is in the
middle, then the above described pro-
dure 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
105 coloured blue-green.

Having now particularly described and
ascertained the nature of our said inven-
tion and in what manner the same is to be
performed, we declare that what we claim
110 is:

1. A process of producing colour
developed reversed images in a three-
layer photographic element of the kind
hereinbefore defined, which consists in
115 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
120 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
125 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
130
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.

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