

[Second Edition.]

PATENT SPECIFICATION

500,793

Convention Date (Austria) : May 9, 1936.

Application Date (in United Kingdom) : May 10, 1937. No. 33290/38.

(Divided out of No. 500,826).

Complete Specification Accepted : Feb. 10, 1939.



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 Ottendorfgasse No. 12, Troppau, (Silesia), Czecho Slovakia, 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 development.

In particular, the invention relates to photographic elements having three differentially colour sensitized silver halide emulsion layers inseparably superimposed on a single support and to processes for producing coloured images in such layers by methods involving selective re-exposure of the layers, that is, the making of positive coloured images by use of the residual silver halide after the usual black development, or of negative coloured images by use of the three silver halide images obtained after general development, fixation and rehalogenisation of the negative silver images. The silver halide in either case has to be independently developed in the respective layers to the corresponding component images. It is known that such independent development of silver halide present in three such layers on a single support presents difficulties which are not encountered in the case of tri-pack material where the emulsion layers are separated for processing. The invention also includes multi-layer photographic elements suitable for the process of the present invention.

According to the present invention there is provided a colour photographic element having three differentially colour sensitized silver halide emulsion layers inseparably superimposed on a single support in which the middle emulsion layer is protected on both sides against the

action of blue light by filter colouring matters which remain after ordinary development or after development and removal of the silver or conversion of the silver to silver salt but are capable of subsequent removal or destruction.

According to one form of the process of the present invention, for producing coloured images in such a photographic element colour component images in the outer emulsion layers are coloured after being made developable by blue light from which the middle emulsion layer is screened by the filter colouring matters and thereafter a colour component image in the middle emulsion layer is made developable and coloured. The silver halide image in the middle emulsion layer may be made developable and coloured in various ways. It may be made developable after development of the outer emulsion layers by prolonged treatment with a vigorous developer or after destruction of the filter colouring matters by exposure to light from either or both sides. The element may be first developed with an ordinary developer and the colour processing is then applied to the residual silver halide, or finely divided silver halide produced therefrom, to produce coloured reversed images. According to another form of the process of the invention, a reversed colour component image in the middle emulsion layer, while still protected by the filter colouring matters, is first exposed from either side to light which is transmitted by such filter colouring matters but which does not affect the images in the other emulsion layers and then developed and processed to colour, whereafter the reversed images in the other emulsion layers are rendered developable, developed and processed to colour. These and other features of the invention will be apparent from the following more detailed description.

If the negative silver is not removed until after reversed colour developed images have been produced in all of the layers or at least in the outer layers it is possible to use an element in which the

[Printed in Great Britain.]

yellow filter colouring matters are resistant only to development.

For convenience we shall first describe the three layer materials, then the three-colour reversal development, and then three-colour redevelopment. The same material can also be used for the making of prints from pictures known under the registered Trade Mark "Autochrome", and also from lenticular screen pictures, especially those of the bi-pack type, and it may be employed for printing from three superimposed latent images by means of three separation negatives or diapositives made from them or from a bi-pack with insertion of the corresponding filter or by projection on the chromosome.

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 emulsions, relatively poor in silver, for three-colour reversal development.

If intermediate layers are provided for the filter colouring matters surrounding the middle layer, strongly-swelling gelatine must be used for these, so that the individual layers are spaced away from one another from each other during the chemical reactions. These filter layers are kept so thin, 0.01 mm. and less, that no undesirable increase of light scattering ensues, despite the fact that they may swell up tenfold. The lower emulsion 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 emulsion layers require developers which intensively dye the image less intensity is required for the lower emulsion layer, since this layer may contain considerably 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, a 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 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 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 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 sensitize to green and yellow but very strongly sensitize to the extreme orange red, in addition to the genuine red, such as 4 : 4¹-dichloro-2¹ : 2¹ : 8-triethylthiacarbocyanine 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 layers is generally necessary for exposure purposes, 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.

The filters with which the present invention is concerned are however provided to facilitate the differential processing of the emulsion layers after exposure and must therefore be stable to the developer (and to mild oxidising agents if the negative silver is removed before colour processing the residual silver halide or if the latent images are developed to silver, and reconverted to silver halide) and capable of removal later by acids, bases, oxidation or reduction.

These filters may be incorporated by various methods.

70

75

80

85

90

95

105

110

115

130

The use of intermediate layers as colour filters is recommended, because strongly-swelling gelatine layers between the silver halide emulsion layers appear necessary for reasons of development-technique.

The whole triplelayer with one or two intermediate layers, or without them, may also be coloured yellow throughout; most simply, by subsequent bathing in dye solutions. It is, of course, essential that the red sensitizer sensitizes exclusively for red and red-orange with a distinct minimum or total lack of sensitivity in the yellow and green region of the spectrum, because yellow and green-yellow rays can then penetrate to the lower, usually red-sensitive layer. The yellow filter dye must not affect the colour sensitivity. In the relatively easily prepared and completely yellow coloured triple layer, the middle emulsion is thus protected from the action of blue light on both sides by yellow filters or yellow colouring of the adjacent silver halide emulsions, enabling blue light to be used for the exposure of regenerated or residual silver halide.

If the present division of the spectrum into three regions is adopted, the amount of filter dye, or the intensity of the colour in all the variations previously described, must be adjusted so that as little as possible, or no blue light at all, reaches the middle layer during exposure.

If the triple layer contains at least one yellow filter layer, or a yellow-dyed blue-sensitive silver halide emulsion layer, bathing of the remaining layers in yellow, red or orange dye solutions, may be done after development.

From the preceding it appears that diffusion of yellow filter dye into the adjacent layers is perhaps without special detriment, but is best avoided in the interest of as true reproduction as possible; the red filter dye must, however, be water-insoluble or non-diffusing. Filter dyes which are insoluble in themselves and strongly coloured substances are added to the gelatine in a highly dispersed state or are precipitated in it. Water-soluble dyes are added to the layers in the form of insoluble salts, or precipitated in the gelatine solution as such. Colouring of the filter layers with water-soluble substantive and high colloidal dyes, is also satisfactory without conversion into the insoluble dye salt. Slight diffusion of the dye is harmless, unless it is capable of sensitizing or reducing the sensitivity. The filter dyes may be precipitated, as described and claimed in application No. 34982/38 (Serial No. 500,795) of even date.

In the selection of appropriate filter dyes, one must take into consideration that

they should be readily washed out or converted into colourless compounds at the end of the colour process by means of acids or bases, oxidizing or reducing agents, or by other suitable reagents. Sometimes, this becomes necessary in an earlier stage of the process in order to make the silver halide layer protected by the filter receptive to blue light, in some cases, after previous bleaching of the silver image situated above it.

Suitable colouring matters are:

1. Insoluble colouring matters which can be synthesised in the gelatine e.g. the azine and phenylhydrazone of alloxan, anils of the hydroxyaldehydes, α -naphthol azo dyes, benzene-azo-phenol, azo-phenol (see Ber. 43/2512), and especially meta-substituted azo-bodies. These are soluble in sodium carbonate and caustic alkali.

2. Basic colouring matters, e.g. auramine (Rowe's Colour Index No. 655), thiaflavine T (Rowe's Colour Index No. 815), nitroso-dimethylaniline, azo-methines, anils and azo-dyes with amino groups in meta-position. These are readily washed out by dilute acids.

3. SPLITTING ANILS and analogously constructed arylated AURAMINES, which may have amino- and dimethylamino groups. Many of these are converted into soluble salts by addition of a bisulphite or thiosulphate.

4. AZOMETHINES, INDOPHENOLS AND INDAMINES. These also are readily split up by dilute acids to form colourless compounds, or are converted into easily washed out salts by addition of a bisulphite or thiosulphate.

5. DIAZO-AMINO COMPOUNDS. These are readily split by acids and the free diazonium salt can usually be easily washed out; those formed from *o-p*-substituted amines are used in order to prevent the possibility of coupling with the oxidation products of the developing agents used.

6. ARYL-AZO-HYDROXY-ANILIDES which are often readily decomposed by acid.

7. COLOURED FERROCYANIDES which are usually split by a dilute solution of sodium carbonate, or caustic alkali or ammonia, and generally also soluble in potassium oxalate or thiosulphate. Suitable are: yellow titanium ferrocyanide, red copper or uranyl ferrocyanide. The colourless ferrocyanides of zinc, thorium etc. are also suitable and can also serve as mordants for yellow and red basic dyes; after destruction or solution of the mordanting bodies, the dyes may be easily washed out.

8. ZINC-MUREXIDE of yellow colour which is easily decolourised by acid. This is prepared by reacting zinc acetate with murexide.

9. **INSOLUBLE COMPLEX COMPOUNDS** which can usually be split by dilute acids with loss of the dye character, including lakes of alizarin dyes and of other hydroxy- and dihydroxy-anthraquinones, often decomposed even by N/10 acid. Other examples of these are:—Complexes of titanic acid with phenols and phenol-carboxylic acids which are precipitated by aromatic bases. Complex salts of copper, nickel and cobalt salts with hydroxy-guanidine, hydroxy-amidine, biformamide, guanyl-formamide, guanyl-urea, nitroso- β -naphthol. Yellow complexes of zinc or cadmium with iso-nitroso-acetophenone. Complex copper and nickel salts of β -naphthaldoxime and analogous compounds which are coloured yellow. Yellow-green to golden yellow complexes of nickel with peonol. Complex salts of *o*-hydroxy-quinoline which are usually entirely insoluble in water, and very easily decomposed by dilute acids; for example, those of magnesium, zinc, cadmium, beryllium and aluminium are yellow, those of titanium and thorium are orange, and the uranyl- and ferrous salts are red, and the copper complex is green.
10. **AZO DYES SPLIT BY REDUCTION** of which examples are insoluble azo dyes or their sulphonic acid salts. These can be split by stannous chloride, sodium hydro-sulphite and various other reducing agents in acid, neutral or alkaline solution, at the azo linkage with loss of the dye characteristics. This treatment is permissible if the component colour images consist of vat dyes, indophenols, azomethines, etc., which are converted into the leuco-form with weak alkaline reducing agents, since leuco-vat dyes are insoluble in sodium carbonate and are easily regenerated by atmospheric oxygen or potassium ferricyanide.
11. **FILTER DYES DESTRUCTIBLE BY OXIDATION.** Examples of these are triphenylmethane dyes, amino-hydroxy-anthraquinones and their sulphonic acid salts, substantive azo dyes or their insoluble or non-diffusing salts, fulgides, isocyanines and other quinoline dyes, which may be very easily destroyed. Dyes with free amino groups are usually not destroyed by acidified nitrite, but a diazonium compound of little affinity to gelatine is formed, so that it can be washed out even more easily than basic dyes.
12. **LIGHT-UNSTABLE FILTER DYES.** Examples of these are iso-cyanines, fulgides and Besthorn's quinaldine acid dyes (Ber. 37, 1237; 41/2002). They may be fairly quickly destroyed by illumination of the finished image with ultra-violet light, which is especially suitable for the yellow filter dye easily accessible from above.
- Dyes of the triphenylmethane series serving as filters and yielding relatively stable leuco-bases, can be left in the image in motion picture films.
- THREE-COLOUR REVERSAL DEVELOPMENT.** 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, amidol, diamido-*o*-cresol, etc. 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 the proper reagents.
- 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 itself (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 it is possible to employ without alteration in the composition of the solution and the development process started or accelerated by warming the layers to room temperature or above.
- Further treatment may be carried out in different ways. The greatest difficulty is to make the residual silver halide of the middle layer developable without influencing the other two existing component images. The advantage of the present invention is that this can be done without necessarily employing sensitizers which withstand the ordinary general development. Since the middle layer is surrounded by two filters which are impermeable to blue light which would affect it, i.e. a yellow and a red or orange one or two yellow ones, blue light can be used to make the residual silver halide of the upper and lower layers developable. The middle component image can be developed by means of energetically acting colour developers. It is, of course, assumed that both filter dyes are stable to the developer and are destroyed only later by acids, bases, oxidation or reduction.
- The residual silver halide is generally directly used for reversal development. It may, however, be first converted into highly dispersed silver chloride as described and claimed in application No. 26472/38 (Serial No. 501,003), if the negative silver has been

removed after the general black development of the latent images. This initially reduced silver can be completely dissolved by oxidizing agents and washed out.

- 5 Examples of methods of carrying out the process of the present invention are as follows :—

EXAMPLE 1.

10 The lower layer is first exposed with blue light after general black development and developed blue-green, and the upper layer then exposed with blue light and developed yellow. Since the primarily reduced silver prevents a complete exposure throughout the depth of the upper layer, some residual silver halide will be left and developed in the colour of the middle layer. It is better, therefore to treat the upper layer, before exposing it to blue light, briefly with a silver solvent dissolving only the silver of the upper layer without allowing it to act on the other two layers.

25 The middle layer is then colour developed with a colour developer which acts so vigorously on addition of ammonia or alkali, or of alcohol or acetone, preferably without air, that the residual silver halide of the middle layer is reduced without exposure after prolonged treatment. This latter treatment is particularly suitable if the middle layer consists of a silver chloride emulsion, (as described and claimed in application No. 13250/37 (Serial No. 500,836) since unexposed silver chloride, although quite stable to the colour developers containing soda necessary for the two outer layers, is more amenable to development without exposure than silver bromide. Even silver bromide can, however, be reduced without pre-treatment or exposure by most leuco-vat dyes in alkaline solution, especially with alcohol or acetone in the solution and the dye formed is precipitated on the image. Residues of the latent images in the two other layers can be destroyed previously by the action of mild oxidizing agents, such as a mixture of potassium ferricyanide and ammonia. A process of colour development with leuco vat dyes is described and claimed in application No. 35101/38 (Serial No. 498,875) of even date.

55 Another way of treating the middle layer is to remove all the silver from the layers and if desired destroy the filter dyes and expose the middle layer from both sides to white, blue or better, ultra-violet light or to soft X-rays and then develop it purple finally removing any silver and fixing out. If desired only one outer layer may be exposed and colour developed before exposure and colour development of the middle layer, if the other filter is left intact. The middle layer may, however, be made developable immediately

after development of the outer layers by exposure from above or both sides to ultra-violet light or to soft X-rays. Finally, the residual silver bromide of the middle layer may be converted into silver iodide or one of its complex salts, if necessary after removal of silver, and coloured purple (or blue-green) by mordanting dyes which are made insoluble before removal of the mordanting agent by suitable precipitants such as phosphotungstates as described and claimed in application No. 35100/38 (Serial No. 500,720).

In the above described processes, it is not necessary for the sensitizers to be stable even to the first development nor in some cases for the filters to be stable to oxidation.

If, however, the yellow-green sensitizer of the middle layer and the filters are stable to development and oxidation then the following procedure can be adopted.

EXAMPLE 2.

90 The metallic silver is removed from all three layers immediately after the usual development. The middle layer can then be exposed from above, or if the lower filter layer is orange from below or from both sides, to yellow light and developed purple. After this the residual silver halide of the other two layers is exposed and colour developed in succession.

Less satisfactory results are obtained if the residual silver halide of the middle layer is first exposed from above to yellow-green light and made developable, then, in any order, the two outer layers to blue light.

If the sensitizers of both lower layers are stable to the developer, the following procedure can be adopted.

EXAMPLE 3.

110 The residual silver halide of the lower layer is made developable by red light and converted into the green-blue component colour image first, then the middle layer is exposed from above to yellow light and developed purple, and finally the upper layer is exposed to blue light and developed yellow. It is, however, more desirable to make the middle component colour image according to the methods previously described.

If the red-sensitive emulsion is in the middle, the procedures described above can be adopted with appropriate changes.

125 Examples of suitable coloured substances into which the silver salt of the middle layer can be converted are to be found in application No. 30655/38 (Serial No. 500,716) of even date.

THREE COLOUR REDEVELOPMENT.

After simultaneous black development of all three emulsions, the element is fixed and the initially reduced silver is con-

70

75

80

85

90

95

100

105

110

115

120

125

130

5
10
15
20
25
30
35
40
45

verted into silver chloride or silver bromide. Each of the two outer emulsions is now exposed to blue light in succession and developed to the appropriate colour, then the middle emulsion is made developable by treatment with thiourea or other fogging agent (see application No. 37123/38 (Serial No. 500,796) of even date) and colour developed, or colour developed without this treatment by means of a vigorously-acting colour developer. Finally, all reduced silver is removed and the filter dyes are destroyed or washed out.

It will be apparent that in this modification the filter colouring matters must be stable not only to the developer but to the oxidising agent for reconvertng the silver to silver halide.

It was found that the yellow-green sensitizers of the middle emulsion, such as erythrosine, rhodamine B and 6G, the dyes "777", "666", "555" (U.S. Specification No. 1,897,866) and numerous other pseudocyanines and pinacyanols are rather difficult to wash out and are stable to mild oxidizing agents, and are also absorbed by reduced silver to such an extent that after the subsequent conversion into silver chloride or silver bromide, certain colour sensitivity remains. The middle layer may, therefore, when such stable sensitizer is used, be exposed to the light to which it is selectively sensitive and developed in colour, then the two outer layers are exposed to blue light, the middle layer being protected by the surrounding filters. In order to make the regenerated silver halide of the middle emulsion accessible to ordinary light, one can also, after colour development of the two outer emulsions, remove the reduced silver and expose the middle layer after removal or destruction of the filters. If desired only one outer layer may be colour developed and treated in this way if the other filter is left intact.

The images obtained are complementary negatives but it is to be observed that the method is applicable to reversal development.

55
60
65

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 colour photographic element having three differentially colour sensitized silver halide emulsion layers inseparably superimposed on a single support in which the middle emulsion layer is protected on both sides against the action of blue light by filter colouring matters which remain after ordinary development, or after development and removal of the silver or conversion of the silver to silver salt.

2. Process for producing coloured images in a colour photographic element as claimed in claim 1 in which colour component images in the outer emulsion layers are coloured after being made developable by blue light from which the middle emulsion layer is screened by the filter colouring matters and thereafter a colour component image in the middle emulsion layer is made developable and coloured.

3. Process for producing coloured images in a colour photographic element as claimed in claim 1 in which a reversed colour component image in the middle emulsion layer is made developable by exposure from either side, while still protected by the filter colouring matters, to light which does not affect the image in the outer emulsion layer or layers and is developed and processed to colour whereafter the reversed colour component images in the outer emulsion layers are made developable, developed and processed to colour.

4. Process as claimed in claim 2 in which the element is first developed with an ordinary developer and the colour processing is applied to the residual silver halide, or finely-divided silver chloride produced therefrom, to produce coloured reversed images.

5. Process as claimed in claim 4 in which the negative silver is removed after the colour processing of the outer emulsion layers.

6. Process as claimed in claim 4 in which the negative silver is removed after the colour processing of all the emulsion layers.

7. Process as claimed in claim 2, in which the colour component images are produced by first developing the latent images to silver, fixing and reconvertng the silver images to silver halide.

8. Process as claimed in claims 2, 4, 5, 6 or 7, in which the image in the middle emulsion layer is developed without exposure by prolonged treatment with a vigorous developer.

9. Process as claimed in claim 4, in which the filter colouring matters are removed or destroyed after colour development of the outer emulsion layers and removal of silver, and the middle emulsion layer is then exposed to light from both sides.

10. Process as claimed in claim 2 or 3, carried out substantially in accordance with any of the foregoing examples.

Dated this 15th day of November, 1938.

W. P. THOMPSON & CO.,
12, Church Street, Liverpool,
Chartered Patent Agents.