PATENT SPECIFICATION

Convention Date (Austria): May 9, 1936.
Application Date in United Kingdom: May 10, 1937.
(Divided out of Application No. 13250/37)
Complete Specification Accepted: Feb. 10, 1939.

500720
35100/38.
(500,826)

COMPLETE SPECIFICATION

Improvements in Processes for the production of Dye Images from Photographic Silver Salt Images

ERRATA

SPECIFICATION No. 500,720.

In the heading on page 1, *insert* "No." *before* "35100/38." *and for* "(Divided out of Application No. 13250/37) (500,826)" *read* "(Divided out of No. 500,826)"

THE PATENT OFFICE,
March 18th, 1939.

emulsion layers ... 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 consists of a not specially colour sensitized silver halide.

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 emulsions, 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 ... 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 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

[Price 4/6]

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Improvements in Processes for the production of Dye Images from Photographic Silver Salt Images

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 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 three colour photography employing elements having three differentially colour sensitized silver halide emulsions on a single support.

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 consists of a not specially colour sensitized silver halide.

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 emulsions, 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 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 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 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

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red, for example 4: 4¹-dichloro-2: 2¹: 8-triethylthiacarbocyanine chloride, can now be made.

In the colour processing of photographic elements having three silver halide emulsion layers on the same support, especially on the same side of the support, by methods involving individual treatment of the layers, the formation of the middle component image offers the greatest difficulty. It is particularly convenient to convert the silver halide in this layer into a mordant for a basic dye. The dye can then be treated with a precipitant therefor, such as a phospho-tungstate, and the silver mordanting compound removed.

This conversion to a mordanting compound is very easy to carry out if the middle layer consists of silver chloride since, in reversal, the residual silver chloride can be used; residual silver bromide is less reactive. This silver chloride can also be converted into silver ferrocyanide which is also a mordant and can in turn be converted into zinc ferrocyanide or copper ferrocyanide or cupric thiocyanate which act still better. It is very advisable to remove all the metallic silver after completion of the two other component-colour images, to reduce the silver bromide of the middle emulsion and to convert it into silver ferrocyanide, by means of potassium ferrocyanide, or a mixture of silver ferrocyanide and lead ferrocyanide by means of one of the known lead intensifiers which is best weakly acidified with acetic acid. The same procedure could be followed in the three-colour development; that is to say by the treatment of images obtained by development of the latent images, fixing and rehalogenisation of the silver. It is, however simpler to convert the metallic silver formed during general black development directly into silver chloride or silver ferrocyanide, after fixing of the residual silver bromide.

The procedure described above is equally applicable to an image of silver chloride, silver ferrocyanide or lead ferrocyanide in the upper layer.

According to the present invention, there is provided a process of three-colour photography wherein three differentially colour sensitized silver halide emulsions on a single support are treated for the production of coloured colour component records in which a silver salt colour component record is converted into a mordant for a basic dye, this is then dyed with a basic dye, then the dye made insoluble by treatment with a precipitating agent and finally the silver mordanting compound is fixed out. Preferably the mordant is produced in the middle layer of a photographic element having three silver halide emulsion layers on a single support.

During conversion of the silver chloride one should take into consideration whether it is located in the upper or middle layer. Conversion before development of the other two emulsions must be done only if the coloured body formed from the silver chloride resists development. This conversion is usually done afterwards and is most reliable if the upper emulsion is silver chloride. If two silver chloride layers are provided, one can be colour developed after exposure and the other one alone converted into a mordanting compound and thence into a coloured image.

The procedure for a two layer element in which one layer consists of a mixture of two silver halide emulsions is similar.

In treating a three layer element of the kind described above, the images in the outer layers may be colour developed by a reversal process or after development, fixing and rehalogenisation of the silver. The residual silver halide (or that obtained by rehalogenisation, as the case may be) of the middle layer can then be converted into silver iodide by bathing in an approximately 1% solution of potassium iodide and this can be dyed with basic dyes, such as rhodamine 6, safranine (Rowe's Colour Index No. 841), methylene blue (Rowe's colour Index No. 922) or similar dyes in 0.1% solution. Any excess of dye can be easily washed out, if necessary with addition of some acetic acid. Fine-grain silver bromide, such as is used in the upper emulsion, is especially suited for use in this process. The dye is then made insoluble by treatment with a precipitating agent such as a phospho-tungstate and the silver mordanting compound fixed out in order to attain greater transparency.

Other precipitants for basic dyes may be used, such as those disclosed in application No. 34982/38 of even date.

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 process of three-colour photography wherein three differentially colour sensitized silver halide emulsions on a single support are treated for the production of coloured colour component records in which a silver salt colour component record is converted into a mordant for a basic dye, this is then dyed with a basic dye, then the dye is made insoluble by treatment with a precipitating agent and

finally the silver mordanting compound is fixed out.

2. Process as claimed in Claim 1 in which the mordant is produced in the middle layer of a photographic element having three silver halide emulsion layers on a single support.

Dated this 1st day of December, 1938.

W. P. THOMPSON & CO.,
Chartered Patent Agents,
12, Church Street, Liverpool, 1.

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