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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Method for the Production of Colour Photographs

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:—

This invention relates to a method for the production of colour photographs in elements having three differentially colour sensitized 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 emulsion 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 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 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 mm. 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 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 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 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

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do not sensitize to green and yellow but very strongly sensitize to the extreme orange red, in addition to the genuine red, for example 4:4¹-dichloro-2:2¹:8-triethylthiacarbocyanine 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 layer between the middle and lower layers is generally unnecessary for exposure purposes, and a red-orange filter layer 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.

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 thinness of the layers, formation of the latent image can take place only in the upper part of each emulsion layer; this effect, however, is mainly noticeable in reversal development, and hardly at all in primary three-colour development and three-colour redevelopment, i.e. development of images which have been obtained by rehalogenising developed and fixed silver images.

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. 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 gelatine 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 two intermediate layers, or without them, may also be coloured yellow throughout; most simply, by subsequent bathing in dye solutions.

In the element having one layer composed of a mixture of two silver halide emulsions and the other layer composed of a not specially colour sensitized silver halide emulsion, the latter layer may be coloured yellow throughout or there may be a yellow filter layer between the two emulsion layers. In such an element the latter layer may be alone on one side of the support and the mixed emulsion layer on the other. In the three-layer element the red or yellow-green sensitive silver halide emulsion layer can be situated alone on the back of the support and the two others on the front.

In the production of three-colour photographs in such elements the coloured component images can be formed of vat dyes.

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 to facilitate subsequent processing. Accordingly, such filter dyestuffs must be resistant at least to the first developer. For example, the middle emulsion layer of an element having three differentially colour sensitized emulsion layers on a single support may be surrounded by filter layers as described and claimed in copending application No. 33290/38.

It has now been found that for these purposes filter colouring matters which are capable of being destroyed or rendered readily removable by oxidation are particularly suitable where the coloured component images are to be formed of vat dyes, which, as is known, are practically stable to oxidation. The indophenols, indamines and azomethines, although they form leuco compounds, are not to be considered as vat dyes within the meaning of the present invention since they are not resistant to oxidation.

According to the invention, the method of producing a colour photograph from an element containing the three primary colour component records in three silver halide emulsions on a single support and containing one or more filter colour matters capable of being destroyed or rendered readily removable by oxidation consists in colouring the colour component records by means of vat dyestuffs and subjecting the filter colouring matters to oxidation. The invention includes the method of producing a colour photograph from an element containing the three primary colour component silver salt records on a single support and containing one or more filter colouring matters capable of being destroyed or rendered readily removable by oxidation which includes developing the silver salt records with leuco vat dyes. Thus the method of producing a colour photograph from an element having the three primary colour component silver salt records in three layers coated on the same support and, in or between some or all of the layers, filter dyestuffs which are capable of being

destroyed or rendered readily removable by oxidation, includes colouring the colour component records in the three layers by independent development thereof with leuco vat dyes.

The destruction of the filter dyestuffs by oxidation may take place simultaneously with the removal by oxidation of silver.

Filter colouring matters which are suitable for the purpose of this invention in that they are resistant to reduction but destroyed by oxidation are well known. It is customary in the textile industry to classify dyes, for the purpose of producing discharge effects, according to their ability to withstand oxidation or reduction. Thus in " Pocket Manual for Dyers, Printers and Paper Makers on the application of the Coal Tar Colours" published by Farbwerke vorm. Meister Lucius und Brüning, of Hoechst on Main in 1911, tables are given on pages 343 to 347 showing the relative resistances to oxidation and reduction of large numbers of dyes. Dyes suitable for the purpose of the present invention can, therefore, readily be found, particularly among the triphenylmethane dyes, the amino-hydroxyanthraquinones and their sulphonic acid salts, substantive azo dyes or their insoluble or non-diffusing salts, fulgides, isocyanines and other quinoline dyes. These may be very easily destroyed by various oxidising agents such as weakly acidified permanganates, persulphates, bichromates, hydrogen peroxide, hypochlorites, or neutral or alkaline potassium ferricyanide. Dyes with free amino groups are usually not destroyed by acidified alkali 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.

The vat dye coloured component images may be produced by development of silver salt images with leuco vat dyes as described and claimed in co-pending application No. 35101/38. The silver can be finally removed by means of Farmer's solution.

The method of the present invention may be applied to the processing of the colour photographic element by reversal or to the processing by primary development of the latent images or to the processing of the images obtained by reconversion of the primarily developed images to silver salt.

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. The method of producing a colour photograph from an element containing the three primary colour component records in three silver halide emulsions on a single support and containing one or more filter colouring matters capable of being destroyed or rendered readily removable by oxidation which consists in colouring the colour component records by means of vat dyestuffs and subjecting the filter colouring matters to oxidation.

2. The method of producing a colour photograph from an element containing the three primary colour component silver salt records on a single support and containing one or more filter colouring matters capable of being destroyed or rendered readily removable by oxidation which includes developing the silver salt records with leuco vat dyes.

3. The method of producing a colour photograph from an element having the three primary colour component silver salt records in three layers coated on the same support and, in or between some or all of the layers, filter dyestuffs capable of being destroyed or rendered readily removable by oxidation, which includes colouring the colour component records in the three layers by independent development thereof with leuco vat dyes.

4. The method as claimed in claim 3, in which the element is one in which the three layers are on one side of the support with the blue component record layer uppermost and the filter dyestuff is a yellow substance present in the upper layer or in an intermediate layer between the upper layer and the other layers.

5. The method as claimed in any of the preceding claims, in which reversed colour component records are coloured with the vat dyestuffs and thereafter the filter colouring matters are destroyed or rendered readily removable by oxidation.

6. The method as claimed in any of the preceding claims in which metallic silver is removed by oxidation after colouring the colour component records and the filter colouring matter or matters is or are destroyed or rendered readily removable by oxidation during such removal of the metallic silver.

Dated this 30th day of November, 1938.

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