PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in and relating to Colour Photography and Colour Cinematography

I, Dr. Bela Gaspar, a Subject of the King of Roumania, of 77/79, Rue Berkendael, (formerly of 42, Avenue Victor Rousseau), Brussels-Forest, Brussels, Belgium, 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 process for the production of multi-colour photographic images. The process according to the present invention consists in effecting the exposure on a multi-layer light-sensitive material having dyestuffs incorporated in some but not all of the layers, transforming the silver images thus produced into a three-colour image in colours other than the natural colours, and then printing this image on to a second multi-layer light-sensitive material having dyestuffs incorporated in some but not all of the layers and finally transforming the image thus produced into a three-colour image, the front layers of the two light-sensitive multi-layer materials used in this process being colourless and blue-sensitive, the second layers in the said materials being yellow and sensitized to green and red respectively in the two materials and the third layers being coloured with that colour which absorbs light rays for which the second layer of the material in question is sensitized and the third layers being sensitized for red and green respectively in the two materials.

Each of the two different light-sensitive multi-layer materials may be used as a recording material for colour photographic exposures, the other one then being used as a copying material for use therewith. One of the features of the present invention lies in the fact that the recording material permits of direct copying on to the appertaining copying material, or that *vice versa* a material similar to this copying material may be employed for the exposure and the resulting images copied on to a material similar to the first-named recording material. In both cases the images produced by the exposure show unnatural colours, but by printing on to the other material colour images are obtained which are true to nature. Moreover, the materials are such that in the taking process they permit of an effective exposure with all rays of light included in the visible spectrum, and accordingly they satisfy all the requirements necessary for a perfect system of colour photography.

The new colour photographic recording material provided by the present invention comprises a plurality of light-sensitive layers, which are arranged on one side or on both sides of a single support, and of which each layer is sensitive in respect of a particular spectral range of the visible spectrum. The combined sensitivity of the whole layers extends over the entire visible spectrum. The single layers which are not situated on the surface, or are not situated on that side which, during the exposure, is directed towards the lens, contain dyestuffs which serve for the formation of the coloured image. The layer which is disposed nearest the lens in the taking process is uncoloured, i.e., transmits light of every wavelength in the visible range.

Of those layers which are further from the lens, the uppermost layer contains a yellow dyestuff, the next one a purple-red or a blue-green dyestuff, viz., a purple-red dyestuff if the layer superimposed thereon is sensitized in respect of green light, and a blue-green dyestuff if the layer superimposed thereon is sensitive to red. As regards the sensitization of the layers, the nature of the material is as follows: the layer directed towards the lens is not specially sensitized in respect of any rays, i.e. is sensitive to blue. The two other layers are sensitized one each in respect of the green and the red spectral ranges.

The copying material for use with this taking material agrees in substance with the recording or taking material. The sensitization, however, of the second and third layers is reversed as compared with the sensitivity of the second and third layers of the recording material. As in the recording material the front layer is colour-

[*Price* 1/-]

less and blue-sensitive, the second layer is yellow-dyed, and the third layer contains either a purple red or a blue-green dyestuff, viz., a purple-red dyestuff if the superimposed layer is sensitized to green light and a blue-green dyestuff if the superimposed layer is sensitized to red.

In the accompanying drawing the arrangement and the nature of the layers are illustrated diagrammatically; Figure 1 shows the one material and Figure 2 the second material for use therewith. In the accompanying drawing, a hatching indicates that the layer does not transmit (i.e., absorbs) rays of the stated spectral range, and the broken lines indicate that the layer is colourless during the exposure and, in the course of the additional treatment, is coloured with a colour which absorbs the rays of the spectral range in question. Crosses indicate the spectral range for which the layer in question is sensitized. The wavelengths are shown from the short wavelengths on the right to the long wavelengths on the left and the vertical lines indicate the separation between the blue, green and red spectral ranges. The arrangement of the material in Figure 1 is accordingly as follows: The uppermost layer 1, which is disposed nearest the lens on exposure, is colourless and is sensitive to blue. After the exposure it is coloured blue-green at the image or non-image parts of the layer, or the whole layer is coloured blue-green and, in this case, a dyestuff picture is produced by destruction of the dyestuff at the image or non-image parts of the layer.

The layer 2 situated immediately under this layer 1 is coloured yellow and is sensitized in respect of green light by means of a known green sensitizer. The yellow colouration of this layer prevents blue light from penetrating into this and the layer immediately under the same.

The next layer 3 is coloured purple-red and is sensitized in respect of red light.

The three layers may be arranged on one or on both sides of a support.

The arrangement and the nature of the layers in the material illustrated in Figure 2 are as follows:—

The top layer 1 which, upon exposure, is located nearest the lens or which, upon copying, is located nearest the source of light, is again colourless and sensitive to blue. After the exposure this layer is coloured purple-red at the image or non-image portions or the whole layer is coloured purple-red and then the dyestuff picture is produced by destruction of the dyestuff at the image or non-image portions.

The layer 2 situated immediately under the layer 1 is also coloured yellow but this layer differs from the corresponding layer 2 of the material according to Figure 1 by its sensitizing and is sensitized in respect of red rays. The yellow colour also in this case prevents the penetration of blue light into the layer 2 and also into the next layer.

The layer 3 located under this layer 2 differs from the third layer of the material according to Figure 1 by other colouration and by other sensitivity, layer 3 being coloured blue-green and being sensitized in respect of the green portion of the spectrum.

For colouring the layers and for sensitizing the same there may be employed suitable dyestuffs which have the appropriate light absorptions and which sensitize the layers in respect of the stated spectral ranges. There may be employed, for example, for colouring the yellow layer Metanil Yellow (Schultz Farbstofftabellen No. 134), for colouring the purple-red layer Diamine Fast Pink, and for colouring the blue-green layer Diamine Pure Blue FF (Schultz i.e. No. 424). It must be understood that these dyestuffs are merely given by way of example, and that there may also be used any other dyestuffs of corresponding colour. Suitable sensitizers are, for example, thioflavine for the green-sensitive layer 2 in Figure 1, or for layer 3 in Figure 2. For the red sensitization there may be employed, for example, ethylviolet for the layer 3, Figure 1, and for the layer 2, Figure 2. Other sensitizers, which produce a corresponding sensitization of the layers may be employed for the layers in Figures 1 or 2.

The dyestuffs in the coloured layers are preferably precipitated therein in the form of non-diffusing salts or insoluble dyestuff compounds. For this purpose there may be employed the already known processes which result in the formation of metallic salts of the dyestuffs, or the formation of insoluble salts of the dyestuffs with inorganic or organic bases or acids. Such methods consist, for example, in the double decomposition of the dyestuff with salts, the anion of the cation of which forms with the dyestuff a non-diffusing compound. Methods of this kind are described, for example, in my prior Specification No. 428,158.

For recording or exposure purposes there is used, for example, the material illustrated in Figure 1, and the colour images thus produced are employed as master images for copying on to the material illustrated in Figure 2.

In order that the nature of the present invention may be the more clearly understood, I will now proceed to describe certain illustrative examples of the same.

EXAMPLE 1.

The material illustrated in Figure 1 is arranged in the camera with the layer 1 located nearest the lens and is exposed. By this means there is produced in each of the layers a latent silver image. Of these silver images that formed in the uppermost layer is produced by the blue points of the object taken; that in the middle yellow-coloured layer is produced by the green rays from the object taken, and that formed in the lowermost layer 3 is produced by the red rays from the object. After the latent images have been developed, the uppermost layer 1 is coloured with a red-absorbing dyestuff, for example, Diamine Pure Blue. The film or the plate is then subjected to the action of a bath of 4% thiocarbamide and 0.1% sulphuric acid and also 0.1% hydroquinone. This bath destroys the dyestuff at the points of the silver in each individual layer, and there consequently remains, after the remaining portion of the silver has been converted by an oxidizing bleaching bath into a silver compound which is capable of being fixed and this silver compound has been fixed by a sodium thiosulphate solution, a pure dyestuff image which is of approximately the following nature. The red points of the original object taken appear green; the blue points of the object taken appear red, and the green points of the original appear blue. If now this coloured master image is copied on to the material illustrated in Figure 2, there passes through the green points of the master image (which are red in the original) green light which acts on the lowermost green sensitive layer 3 of the copying material illustrated in Figure 2. Red light passes through the red points of the master image and acts on the yellow middle layer 2, Figure 2. There are accordingly reproduced in the same the blue points of the original since the parts of the master image which are coloured red correspond to the blue portions of the object taken. Similarly light passing through the blue points of the master image (which are green in the original) produces a silver image in the colourless layer 1 in Figure 2.

After the development of the latent images the uppermost layer 1 is coloured with a purple-red, i.e., green-absorbing dyestuff, for example, Diamine Fast Pink, and the fixed film is treated in exactly the same manner as the recording film illustrated in Figure 1. After the destruction of the dyestuff at the points of the silver image in each individual layer, and after the removal of the silver, there remains a pure dyestuff image, the nature of which is as follows: At the points where the blue-green dyestuff has been destroyed in the lowermost layer (these in the original are the red points and in the master image the green points) red is produced by the subtractive combination of the dyestuffs present in the two other layers. Where the yellow dyestuff has been destroyed in the middle layer 2, Figure 2 (these in the original are the blue points and in the master image are the red points) the remaining dyestuffs in the two other layers result in a subtractive blue. Finally where the purple-red dyestuff has been destroyed in the uppermost layer 1, Figure 2 (these in the original are the green points and in the master image are the blue points) there results from the dyestuffs of the two other layers a subtractive green. Comparison between the colours of the object taken and those of the finished image shows complete identity.

Exactly the same result is obtained if the material illustrated in Figure 2 is used for recording purposes and the material illustrated in Figure 1 is used as the copying material. The conditions are explained by the following Example 2: The blue points of the original are recorded in the uppermost colourless layer in the form of a latent silver image; the green parts of the original are recorded in the lowermost blue-green coloured layer 3, Figure 2, and the red rays are recorded in the red-sensitive layer 2, Figure 2. The treatment of the latent images, the fixing of the image and the colouring of the uppermost layer 1, Figure 2, is performed in the same fashion as in Example 1, the uppermost layer being coloured with a purple-red dyestuff, for example, Diamine Fast Pink, which absorbs in the green spectral range. The additional treatment by destruction of the dyestuff and removal of the silver also takes place in the manner described in Example 1. There is obtained by the exposure and the measures described a pure dyestuff image, the nature of which is as follows:—The red points of the original appear blue; the blue points of the original appear green, and the green points of the original appear red.

If now this coloured master image is copied on to the material illustrated in Figure 1, there passes through the blue points of the master image (the red points in the original) blue light which acts on the uppermost layer 1, Figure 1. Through the green points of the master image (the blue points in the original) there passes light which acts on the layer 2, Figure 1. Through the red points of the master image (the green points in the original) there passes light which produces a silver image in the lowermost layer of the copying material according to Figure 1.

After the latent images have been developed the uppermost layer 1, Figure 1, is coloured with a blue-green dyestuff, and after this the procedure is exactly the same as already repeatedly described.

Where the blue-green dyestuff of the uppermost layer has been destroyed, that is, at the blue points in the master image (the red points in the original) the colours of the remaining layers supplement each other subtractively to form red. Where the yellow dyestuff of the middle layer has been destroyed, at the green points in the master image (the blue points of the original) the remaining colours supplement each other to form a subtractive blue. Finally, where the purple-red colour of the lowermost layer has been destroyed, that is, at the red points of the master image (the green points in the original) the undestroyed colours of the two other layers supplement each other to form green. The result, therefore, also when changing about upon the exposure and the copying process the two materials shown in Figures 1 and 2, is finally a multi-colour image in true colours though the intermediate master image is different from that produced by Example 1.

By employing the two corresponding materials according to Figures 1 and 2 it is also possible to obtain images which are correct in colour if, for destroying the dyestuff in the individual layers, there are employed baths which do not destroy the dyestuff, as above described, at the points of the silver deposit, but at the unexposed points of the individual layers. This may be performed by using a material as illustrated in Figure 1 for the exposure and a material according to Figure 2 as copying material, or *vice versa* in such fashion that the exposure is made on to a material as illustrated in Figure 2 and the material illustrated in Figure 1 is employed as copying material. The first of these possibilities is described by way of example in the following Example.

EXAMPLE 3.

The recording material is the material illustrated in Figure 1. In this material there are produced, upon the exposure, three silver images in the individual layers and the uppermost layer is coloured blue-green as in Example 1. The destruction of the dyestuff is effected in the known manner by treatment in a bath which destroys the dyestuff at the unexposed points but not at the points of the silver, for example by means of the reagents described and claimed in my prior patent No. 395,718.

The images are freed from silver in the known manner. The result is a master image of the following nature. The green points of the original are coloured yellow, the blue points of the original are coloured blue-green, and the red points of the original are coloured purple.

This master image is employed for copying on to the material illustrated in Figure 2. The yellow points of the master image transmit no blue light, and accordingly the parts of the blue-sensitive layer situated below the yellow points of the master image (the green points of the original) are not exposed and upon the subsequent destruction of the dyestuff there will be destroyed at these points the purple-red dyestuff in the layer 1, Figure 2. These points, by reason of the subtractive combination of the blue-green and yellow colours in the two other layers of the copying material appear green, as at the corresponding point of the object taken. The blue-green colouring of the master image also prevents an exposure of the red-sensitive layer 2, Figure 2, at those points which correspond with the blue points of the original and accordingly, upon the destruction of the dyestuff at the unexposed points of the layer 2, the blue-green and the purple-red dyestuffs remain visible after destruction of the yellow dyestuff and combine substractively to form blue. The position is exactly the same in the case of the purple-red points of the master image, which correspond with the red points of the original, and which, since the same prevent exposure of the green sensitive layer 3, Figure 2, cause the removal of the blue-green dyestuff from the layer, so that the corresponding points, by reason of the substractive combination of the purple-red and yellow colours present in the other layers, result in a pure red, which coincides with the corresponding points of the object taken.

In all of the examples described in the above the colourless upermost layer has been coloured diffusely, and the dyestuff has been destroyed at the image or non-image portions simultaneously with the treatment of the remaining layers. In order to fix this diffuse colouring of the uppermost layer in the layer, it is desirable to add to the layer a precipitating agent for the dyestuffs which are subsequently applied. Thus, for example, the uppermost colourless layer has added thereto 3 grammes of diphenyl guanidine per square metre of the surface of the layer, the base being added as such or in the form of a salt to the emulsion prior to pouring. Alternatively, the layer may be treated after the pouring thereof on to the support or after exposure, with a solution of the precipitating agent. Another precipitating agent for Diamine Fast Pink G is, for example, lactic quinine, which may likewise

be incorporated in the emulsion or in the layer. Other precipitating agents are described in my co-pending Application No. 17299/36 (Serial No. 478,735).

In place of the diffuse colouring with subsequent destruction of the dyestuff at the image or non-image portions the colourless layer may also be coloured in the known fashion at the exposed or at the unexposed points, the known mordanting and tanning processes being suitable for this purpose, the dyestuff then being subsequently applied and fixed either at the mordanted or tanned parts of the layer. If the dyestuff is destroyed at the points free of silver in the underneath layers, the points of the silver are coloured in the colourless layer, for example, by converting the silver deposit into a silver compound which acts as a mordant for dyestuffs, or the silver image may be converted into a Prussian blue image.

EXAMPLE 4.

As the recording or copying material there is employed the material illustrated in Figure 1. After exposure, developing and fixing of the three-part-images in the single layers the material is subjected to a treatment with a solution of :—

4 grams. potassium bromate.
10 grams. soldium chlorate.
5 grams. hydrochloric acid.
200 grams. water.

The dyestuff is destroyed at the points free of silver and at the same time the silver is converted into a silver salt capable of being fixed. After rinsing, but prior to fixing, the film is bathed in a solution of 25 grammes ferricyanide of potassium and 5 grammes potassium iodide in 1000 grammes of water, rinsed for a short time and then coloured with Virage Blue-green (Agfa). The colouring process is stopped at the appropriate stage as soom as the image has taken up a sufficient quantity of dyestuff in any suitable way, for example, by removal from the dyestuff solution and immersion in water, the silver salt being subsequently dissolved out of all layers, for example, by sodium thiosulphate solution.

It is also possible for the purpose of colouring the colourless upper layer to produce the dyestuff locally at the image or non-image portions or in a diffuse manner from dyestuff components which are contained in the layer or which are incorporated therein by bathing, said dyestuff components being practically colourless themselves.

EXAMPLE 5.

After all part-images have been produced, developed and fixed in the material illustrated in Figure 1 the dyestuff of the two underneath layers is destroyed at the points of the silver by treatment with an aqueous solution of 5% thiocarbamide. The uppermost layer, the emulsion of which has added thereto the leuco compound of tetrabromindigo, is treated in a solution comprising 0.2% potassium bichromate and 2% of 20% sulphuric acid. By this treatment the dyestuff is produced at the points free of silver.

The present invention is concerned with the production of copies from coloured master images as well as the production of exposures in the camera, and in particular it enables coloured images which have been produced on the copying material to be copied quite readily on a material which agrees in its nature with that which has served as master image. For example, a coloured image true to nature, which has been produced on the material illustrated in Figure 2 with the use of a master image according to Figure 1, may again be re-copied on to the material illustrated in Figure 1, and the coloured image thus obtained can be employed in turn for producing any desired number of copies on the material illustrated in Figure 2. Additional advantages are obtained from the possibility of interchanging recording and copying material as desired.

The light-sensitive multi-layer materials used in carrying out the present invention and as illustrated in Figures 1 and 2 of the drawings form the subject-matter of my co-pending Patent Application No. 7081/38 (Serial No. 483,463), and no claim is made herein to such material *per se*.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is :—

1. A process of producing multi-colour photographic images which consists in effecting the exposure on a multi-layer light-sensitive material having dyestuffs incorporated in some but not all of the layers, transforming the silver image thus produced into a three-colour image in colours other than the natural colours, and then printing this image on to a second multi-layer light-sensitive material having dyestuffs incorporated in some but not all of the layers and finally transforming the image thus produced into a three-colour image, the front layers of the two light-sensitive multi-layer materials used in this process being colourless and blue-sensitive, the second layers in the said materials being yellow and sensitized to green and red respectively in the two materials, and the third layers being coloured with that colour which absorbs light rays for which the second layer of the material in question is sensitized and the third layers being sensitized for red

and green respectively in the two materials.

2. Process as claimed in Claim 1, characterised in that the top layer is diffusely coloured at a point in the process after exposure, the dyestuff being destroyed simultaneously with the selective destruction of the dyestuffs in the other layers.

3. Process as claimed in Claim 1, in which the coloured image in the top layer is produced by application of the dyestuff at the image or non-image parts of the layer, for example, by means of a toning process or a mordanting or tanning process with subsequent application of the dyestuff.

Dated this 16th day of July, 1936.

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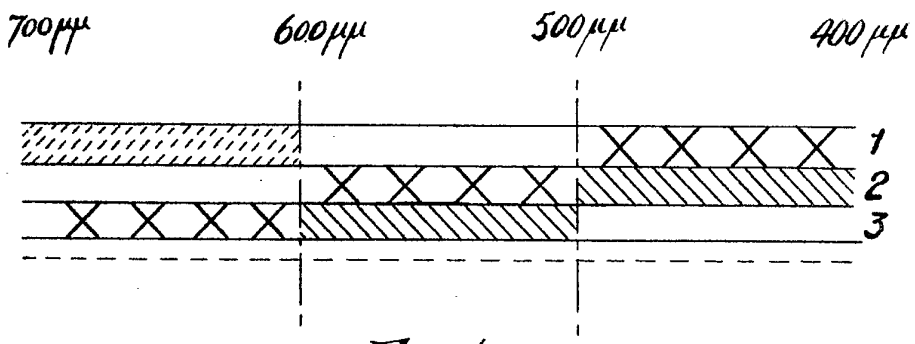

Fig. 1.

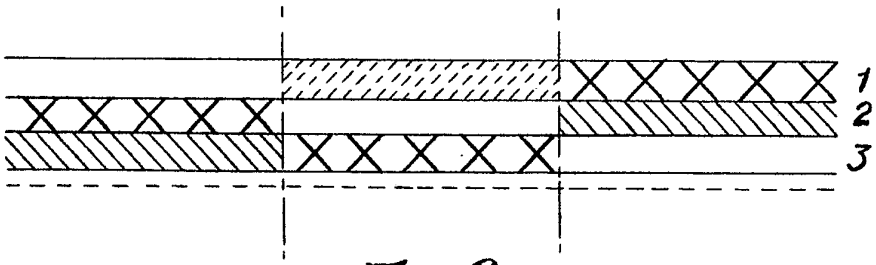

Fig. 2.

Malby & Sons, Photo-Litho