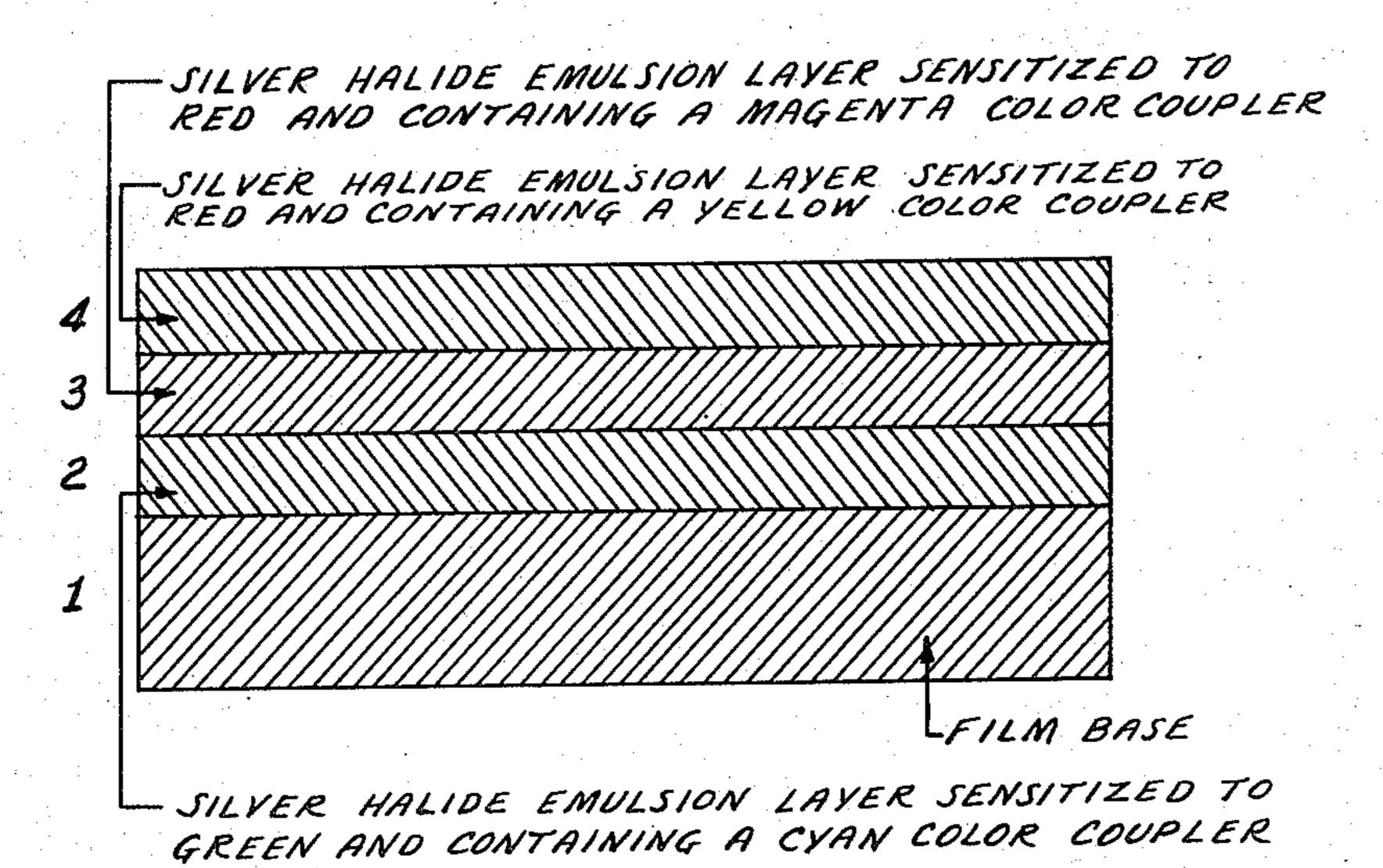
## H. VON FRAUNHOFER ET AL

COLOR PHOTOGRAPHIC ELEMENT Filed March 31, 1949



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#### COLOR PHOTOGRAPHIC ELEMENT

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2 Claims. (Cl. 95—2)

The present invention relates to the production of coloured photographic images, particularly to the production of images giving the impression of trichromatic images from bi-colour negatives, and comprises processes for the production of such images, the photographic materials employed therein and the coloured images obtained thereby.

Colour photographic processes are known wherein the light and dark areas of at least one 10 of the separation images, constituting a positive colour image, are differently coloured, either by toning, mordanting, silver dye bleach, imbibition or colour development processes.

In one known colour photographic process, for example, two positive prints obtained from two component negatives are each dyed with a different combination of dyes which are so chosen that on subsequent washing or treatment in a weak solution of a reducing agent they will be 20 retained in the prints in accordance with the gradation of light and shade.

Bi-colour images having a great similarity with tricolour images may also be obtained by using halide layer containing a plurality of dyes which possess varying powers of resistance against solvents or reagents.

In application Serial No. 73,799, now U.S. Patent No. 2,568,208, there has been proposed a 30 negative-positive colour development process which allows the printing from a bi-colour negative image of an approximately true-coloured image, giving a trichromatic impression. In this process the negative photographic material com- 35 prises a support coated with a red-sensitive silver halide emulsion layer containing a colour coupler, e. g. magenta, a yellow filter layer and an orthochromatic silver halide emulsion layer containing a colour coupler, e. g. cyan. Optionally, plain 40 gelatine layers are coated between the yellow filter layer and the adjacent layers, and an antihalation layer is coated upon the support which may be of a temporary character, constituting a stripping base. The positive material comprises 45 a support which is coated with an orthochromatic silver halide emulsion layer containing a colour coupler, e. g. cyan, and a red-sensitive silver halide emulsion layer containing a colour coupler, e.g. magenta. Optionally, an anti-halation layer 50 is coated upon the support and a plain gelatine.

intermediate layer between the two emulsion layers. The negative, complementary coloured image obtained in the said negative material is printed on the said positive material. In order to obtain by this process a coloured image, giving the impression of a trichromatic image, a yellow colour coupler was added to the colour developer used for developing the cyan and magenta coloured images in the positive material. The aim of this procedure was to produce in the upper emulsion layer at the same time a magenta and a yellow colour. In practice, the production of yellow colour is not limited to the upper layer but yellow is produced also in the bottom layer, especially where no development takes place in the corresponding areas of the upper layer.

According to the present invention, at least one separation image of the colour photographic negative is printed onto two layers of the positive stock which have at least partially the same spectral sensitivity but contain different colour couplers.

The speed of these layers having at least partially the same spectral sensitivity may be the a photographic material having at least one silver 25 same or different as circumstances may require the production of equally strong or unequally strong images in these layers.

The production in one layer of an image which is stronger than the image produced in the other layer may easily be effected by making the former layer sensitive to a broader spectral region, so that light of a small spectral region will expose one layer but not the other.

The most striking effect obtainable by the process according to the present invention is a different colouring of the lighter and the darker areas of the image constituted by the partial images produced in the two layers having at least partially the same spectral sensitivity. For this purpose the upper of these layers, or the layer having the higher speed, shall contain a colour coupler required for the light areas, while the lower or the slower layer shall contain a colour coupler which will produce a dye which in combination with the dye produced in the other layer will give the colour required for the dark areas.

The relation between the two amounts of colour produced in each of the layers having approximately the same sensitivity may be influenced by printing through an appropriate colour filter. If the two colours produced are e. g.

In one embodiment of the present invention, the negative colour image obtained on the photographic material described above is printed onto a positive photographic material which comprises 10 a support coated with three light-sensitive silver halide emulsion layers, the two upper layers of which are sensitised approximately to the same region of the spectrum (green or red). The upper of these two layers contains a yellow col- 15 our coupler while the other contains a magenta colour coupler and the upper layer preferably has a higher speed than the other. The third emulsion layer is sensitised to another region of the spectrum (red or green) and contains a cyan col- 20 our coupler. Water-permeable plain colloid (e. g. gelatine) intermediate layers may be coated between the said emulsion layers and an antihalation layer may be coated on the support. As a result of this process, the less exposed parts of 25 the image produced in the upper layers are yellow, while the more exposed parts are coloured with a mixture of yellow and magenta colours.

The photographic material used according to this embodiment is illustrated in the accom- 30 panying drawing. In this material a support 1 such as the usual film base carries three photographic silver halide emulsion layers 2, 3 and 4. Layer 4 is sensitized to red and contains a coupling material developable to yellow. Layer 3 35 is sensitized to red and contains a coupling material developable to magenta. Layer 2 is sensitized to green and contains a coupling material developable to cyan.

A bicolour process according to the present invention is to be preferred to other bicolour processes, since it produces a trichromatic effect in a quite simple way. In comparison with a tricolour process, it offers the advantage of being less expensive and easier, especially in the selection of the appropriate printing filter. The negative material which may be used in such process has higher speed and is less expensive than negative tricolour photographic material. Especially, because of the high speed of the negative material used, such process is particularly adapted for the production of news reels.

The present invention is illustrated but in no way limited by the following example:

A photographic film comprises a support coated with two bromo iodide negative type emulsion layers separated by a colloidal silver yellow filter layer, the lower emulsion layer being sensitised to red by incorporation of a dye such as for example that disclosed in French Patent No. 60 890,833 having the following structural formula:

and containing a coupler such as one having the following structural formula:

The upper emulsion layer is sensitized to green by incorporation of a dye such as for example that disclosed in British Patent No. 496,116 having the structural formula: III

$$C_{2H_{5}}$$
 $C_{2H_{5}}$ 
 $C_{2H_{5}}$ 
 $C_{2H_{5}}$ 
 $C_{2H_{5}}$ 
 $C_{2H_{5}}$ 

and containing a coupler such as one having the following structural formula:

accompanying Formula I (French patent specification No. 890,833) and containing the coupler according to the accompanying Formula II, the upper emulsion layer being sensitised to green by the dye according to the accompanying Formula III (British patent specification No. 496,116) and containing the coupler according to the accompanying Formula IV. This film is exposed in the camera and processed as follows:

- (1) Developed for 10 minutes in a solution obtained by mixing the following solutions 24 hours before use:
  - A. N,N diethyl p phenylene diamine sulphite \_\_\_\_\_g 2.75

    Water to 200 ccs.

    B. Sodium sulphite \_\_\_\_\_g 4

    Potassium carbonate \_\_\_\_\_g 75

    Potassium bromide \_\_\_\_\_g 0.5

    Hydroxyl-amine hydrochlo
    ride \_\_\_\_\_g 1.2

    Water to 800 ccs.
- (2) Treated for 3 minutes in a stop bath containing 17.3 g. sodium acetate and 12.7 g. acetic acid in 1000 ccs. of water.
- (3) Hardened for 5 minutes in a bath containtaining 30 g. chrome alum in 1000 ccs. of water,
- (4) Washed for 15 minutes,

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Treated for 8 minutes in a bleach bath containing 100 g. potassium ferricyanide, 5.2 g. disodic phosphate in 1000 ccs. of water and containing also 3 ccs. sulphuric acid for each 5000 ccs. bath,

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- 5

- (6) Washed for 5 minutes,
- (7) Fixed for 5 minutes in a bath containing 300 g. sodium thiosulphate and 20 g. sodium sulphite in 1000 ccs. of water,
- (8) Washed for 5 minutes,
- (9) Treated for 5 minutes in a bath containing 12.5 ccs. of an aqueous solution of formaldehyde 40% and 25 g. sodium carbonate in 1000 ccs. of water in order to stabilise the dyes, and finally
- (10) Washed for 15 minutes.

The negative thus obtained is copied onto a photographic film comprising a support coated with three bromo iodide positive type emulsion layers, the lower emulsion layer being sensitised 15 to green by means of the above identified green sensitizing dye III, and containing a coupler such as one having the structural formula:

the middle emulsion layer being sensitized to red by means of a dye such as that disclosed in United States Patent No. 2,276,554, having the formula: 30

### VI

and containing a coupler having the Formula II above, and the upper emulsion layer being sensi-

o e according to

tised to red by the dye according to the above mentioned Formula VI and containing a coupler having the formula:

VII

The positive film thus exposed is developed and further treated in the same manner as the negative, except that in the developing solution the amount of potassium bromide is increased to 2.5 g.

#### We claim:

1. A photographic material comprising an assembly of a plurality of light-sensitive layers including a first red-sensitive layer containing a coupling material developable to yellow, a second red-sensitive layer containing a coupling material developable to magenta, and a bluegreen-sensitive layer containing a coupling material developable to cyan, the layer containing the yellow coupler having a higher speed than the layer containing the magenta coupler.

2. A photographic material as defined in claim 1 wherein the assembly includes a blue-green sensitive layer containing a coupling material developable to magenta.

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