

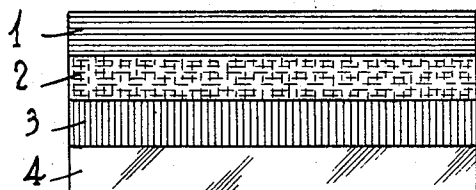
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2,283,361

COLOR-PHOTOGRAPHIC MATERIAL

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*Highly sensitive to blue.*

*Very low inherent blue sensitivity  
and sensitized to green.*

*Highly sensitive to blue.*

*Support.*

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## UNITED STATES PATENT OFFICE

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## COLOR-PHOTOGRAPHIC MATERIAL

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This invention relates to a color-photographic material with different superimposed layers.

In earlier patents photographic multilayer materials have been described in which the dye necessary for the formation of the image is present before the exposure in at least one of the light-sensitive layers. Not only does this dye build up the finished image but it also acts as a filter dye in that it transmits only those light rays that are to form a latent image in the layer itself and those light rays that might be required for the exposure of a layer lying behind, while simultaneously screening the layer in which it is present against the action of certain rays of light.

Thus, for example, the yellow dye in the red sensitive layer of the material described in U. S. Patent No. 1,985,344 dated December 25, 1934, protects this layer from the effect of the blue light. In the material described in U. S. Patent No. 2,183,394 dated December 12, 1939, the yellow dye protects the green sensitive layer from the blue light, and in the material described in U. S. Patent No. 2,183,393 dated December 12, 1939, Fig. 2, the yellow dye present in the infrared sensitive middle layer acts as a protective filter limiting the effect of the exposure to blue light to the two outer layers.

It has been found that if the yellow dye is present only in the concentration necessary for the production of a multicolor image, it will not in all cases be high enough to prevent sufficiently the entry of blue light into the layer. Therefore, it is an object of the present invention to improve the colour separation by avoiding the disturbing effect of the light entering and exposing a layer of complementary color. This is the more desirable if the images are not only to be projected directly, in which case the human eye would hardly discover any shortcomings in the multicolor image, but also if they are to serve for the production of prints. Conditions similar to those described above the also encountered if a layer is sensitized panchromatically and if it contains a magenta dye that does not suffice for the complete exclusion of the green rays.

The present invention has for one of its objects the improvement of the color separation of the individual color selection images. This is achieved by using emulsions which show large sensitivity differences among each other with respect to that light for which the sensitivities of the layers overlap each other. The color photographic multilayer material according to the present invention comprises at least one colored

silver halide emulsion layer that is sensitive to light rays used in the exposure of a superimposed layer and which is dyed with an image-forming dye absorbing such light rays, the said colored silver halide layer being formed by an emulsion which in its uncolored state possesses, as compared to the emulsions used for the other layers, a considerably lower sensitivity to the light rays absorbed by the dye used for coloring the layer, and being additionally sensitized for light rays which are capable of passing through the said colored layer and also through the superimposed layer or layers. Thus in the case in which the yellow-dyed layer does not offer sufficient protection against undesired exposure during the exposure to blue light of a preceding blue-sensitive layer, this yellow layer is produced from the emulsion of least sensitivity. Therefore, the least sensitive emulsion is dyed in this case with a yellow dye which is resistant to the usual photographic treatment baths but can be locally destroyed in proportion to the developed silver image, by a process of the kind described in U. S. Patent No. 2,020,775 dated November 12, 1935. This yellow-dyed emulsion is sensitized for green, red or infra-red light by adding the sensitizing dyes known for this purpose.

The sensitivity of the yellow layer thus obtained is considerably less than the blue sensitivity of the other layers in view of the small inherent sensitivity of the emulsion. Accordingly if, for example, the multilayer material is exposed to the white light of a half-watt bulb the blackening thereby obtained in the yellow emulsion sensitive for green or red light is considerably less than the blackening simultaneously obtained by the same light in the other layer formed by a blue sensitive emulsion whose inherent sensitivity is very much greater than the inherent sensitivity of the emulsion used for producing the yellow-dyed emulsion layer. On the other hand, however, the blue sensitivity of the yellow-dyed layer is so small on account of the choice of the weakly sensitive emulsion and, on account of the addition of the yellow dye, is kept so low that the blue rays which are necessary for sufficient and thorough exposure of the blue sensitive layers are not capable of producing any appreciable light impression in the yellow-dyed layer.

During the production of pictures—unless a very strong yellow filter were used in front of or in the blue sensitive front layer—such a material would give an especially strongly blackened image of the blue color selection in comparison

to the two other selections, but the blue picture would actually remain limited to the front layer.

The material described is, however, especially suitable for the production of prints. Here the full sensitivity of the emulsions can be utilised to the fullest advantage and the individual component images can be obtained in the individual layers with an equal or a balanced blackening if the low sensitivity of the yellow-dyed layer is equalised by means of stronger exposure or if a printing light is used in which those rays of light are predominant by which only the weakly sensitive layer is affected. If used in this manner, the material has the advantage of allowing a very sharp color separation between the individual layers, as the printing light used for the outer layers can not affect even the surface of the layer lying behind.

When using a multilayer material comprising one layer which in comparison with the other layers is prepared from an emulsion of lower inherent sensitivity and when developing the latent images in the different part layers by a common development, images in the different part layers may sometimes be obtained which deviate from each other as regards their gradation. Thus in the blue sensitive layer whose inherent sensitivity is high, an image of low contrast may be obtained; on the other hand, in the red sensitive layer whose inherent sensitivity is smaller than that of the blue sensitive layer and in which even the sensitizer does not raise the sensitivity very much, an image of high contrast is obtained. These differences in gradation are of minor importance in the case of an exposure material, because during the production of the individual color-component prints from the exposure material the differences can be equalised again by simply changing the developing conditions of the prints. If the multilayer material is used as a printing material the gradation differences of the various layers can be taken into account by using a printing master or masters that individually are adapted to the gradation of each printing layer. In other cases if the dyes are properly chosen in spite of the different gradation of the silver images, all of the dye images in the various layers can be made to show substantially the same gradation. For the production of the dye images the methods of the local dye destruction described in prior patents, for example in Patent No. 2,020,775 dated November 12, 1935, are especially suitable. For example, an acid thiocarbamide solution or an aqueous hydrochloric acid solution can be used.

*Example.*—As shown in the drawing three silver bromide gelatine emulsion layers 1, 2 and 3 are arranged upon one or upon both sides of the transparent support 4. The middle layer 2 which is to receive the print of the blue color sensation record is prepared from an emulsion which in comparison to the two emulsions used for the other layers has an inherent blue sensitivity which is about 1/10th of the inherent blue sensitivity of these other emulsions. For example, the emulsion used for the middle layer 2 is an unripened silver bromide gelatine emulsion, whereas the emulsion used for the other two layers is a ripened emulsion. The unripened emulsion is dyed with Chrysophenine G (Schultz Farbstofftabellen, Leipzig 1931, 7th edition, volume 1, No. 726) and 1.2 gram of the dyestuff are used per sq. m. of the surface of the layer. The emulsion is also treated with triphenylguanidine lactate in order to bring the yellow

dyestuff into the insoluble form. The emulsion further contains erythrosine as a sensitizer for green. The two outer layers 1 and 3 are not especially sensitized and therefore have only their inherent blue sensitivity. One of these layers, i. e. 1, which is to receive the print of the red color sensation record, may be dyed with a blue-green dyestuff as Pontamine Sky Blue 6 B (Schultz Farbstofftabellen I. c. No. 510), the other one, i. e. 3 which is to receive the print of the green color sensation record, may be dyed with a magenta dye, such as Tuchehtbrillantrot 2 B (Schultz Farbstofftabellen, Leipzig 1932, 7th edition, volume 2, page 221) or Chloraminbrillantrot 8 B (Schultz Farbstofftabellen, Leipzig 1931, 7th edition, volume 1, No. 425). If none of the other layers or if only one of them besides the yellow-dyed layer is dyed, then one of them can also be sensitized for red light. In these cases all three layers can be exposed from the side of the blue sensitive layer. Otherwise, if the two outer layers are only blue sensitive the material is exposed from both sides. In the cases in which the exposure is possible from one side, also paper can be used as a support, all of the layers then being coated on top of each other, with the interposition of plain gelatine layers if desired.

What is claimed is:

1. A multilayer light sensitive material for color photography comprising a plurality of superposed silver halide emulsion layers predominantly sensitive to different parts of the spectrum, at least one silver halide emulsion layer being colored by a dyestuff which is not removable by ordinary photographic treating baths but which is selectively removable under the influence of a silver image and which transmits light rays to which the layer itself is predominantly sensitive, another of said layers superposed with respect to said colored layer being transmittant for and predominantly sensitive to light rays absorbed by said dyestuff but transmittant for and insensitive to light rays for which said colored layer is predominantly sensitive, said layers being basically of the same silver halide, so that they have substantially the same natural spectral sensitivity range, said colored layer having, before coloring, a speed so considerably lower than said superposed layer within said range, that the light rays within said range which are necessary for sufficient and thorough exposure of said superposed layer are not capable of producing any appreciable light impression in said colored layer.

2. A light sensitive material for producing multi-color images comprising a transparent support and three light sensitive silver halide emulsion layers, the two outer layers being of the same predominant sensitivity, the middle layer being predominantly sensitive for another part of the spectrum, each of the outer layers being transmittant for the light rays for which the layer is predominantly sensitive, and at least one of the outer layers being insensitive to and being transmittant for light rays for which the middle layer is predominantly sensitive, the middle layer being colored by a dyestuff which is not removable by ordinary photographic treating baths but which is selectively removable under the influence of the silver image and which transmits light rays for which the layer itself is predominantly sensitive but absorbs light rays to which both the outer layers are predominantly sensitive, at least one of said outer layers and

said middle layer being basically of the same silver halide, so that they have substantially the same natural spectral sensitivity range, said colored middle layer having, before coloring, a speed so considerably lower than said last mentioned outer layer within said range, that the light rays within said range which are necessary for sufficient and thorough exposure of said last mentioned outer layer are not capable of producing any appreciable light impression in said colored middle layer.

3. A multi-layer light sensitive material for color photography comprising a plurality of superposed silver halide emulsion layers predominantly sensitive to different parts of the spectrum, at least one silver halide emulsion layer being colored yellow by a dyestuff which is not removable by ordinary photographic treating baths but which is selectively removable under the influence of a silver image and being predominantly sensitive to a spectral range other than blue, another of said layers superposed with respect to said colored layer being transmittant for and predominantly sensitive to blue light rays but transmittant for and insensitive to the spectral range for which said yellow layer is predominantly sensitive, said layers being basically of the same silver halide, so that they have substantially the same natural blue sensitivity range, said yellow layer having, before coloring, a speed so considerably lower than said superposed layer within said blue range, that the light rays within said blue range which are necessary for sufficient and thorough exposure of said superposed layer are not capable of producing any appreciable light impression in said yellow layer.

4. A light sensitive material for producing multi-color images comprising a transparent support and three light sensitive silver halide emulsion layers, the two outer layers being predominantly sensitive to blue light, the middle layer being predominantly sensitive for another part of the spectrum, each of the outer layers being transmittant for the light rays for which the layer is predominantly sensitive, and at least one of the outer layers being insensitive to and being transmittant for light rays for which the middle layer is predominantly sensitive, the middle layer being colored yellow by a dyestuff which is not removable by ordinary photographic treating baths but which is selectively removable under the influence of the silver image, at least one of said outer layers and said yellow middle layer being basically of the same silver halide, so that they have substantially the same natural blue sensitivity range, said yellow middle layer having, before coloring, a speed so considerably lower than said last mentioned outer layer within said blue range, that the light rays within said blue range which are necessary for sufficient and thorough exposure of said last mentioned outer layer are not capable of producing any appreciable light impression in said yellow middle layer.

5. A multi-layer light sensitive material for color photography comprising a plurality of superposed silver halide emulsion layers predominantly sensitive to different parts of the spectrum, at least one silver halide emulsion layer being colored yellow by a dyestuff which is not removable by ordinary photographic treating baths but which is selectively removable under the influence of a silver image and being predominantly sensitive to a spectral range other than blue, another of said layers superposed with respect to said colored layer being transmittant for and predominantly sensitive to blue light rays but transmittant for and insensitive to the spectral range for which said yellow layer is predominantly sensitive, said layers being basically of the same silver halide, so that they have substantially the same natural spectral sensitivity range, said colored layer having, before coloring, a speed so considerably lower than said superposed layer within said range, that the light rays within said range which are necessary for sufficient and thorough exposure of said superposed layers are not capable of producing any appreciable light impression in said colored layer, said colored layer being formed by an unripened emulsion and said superposed layer being formed by a ripened emulsion.

6. A light sensitive material for producing multi-color images comprising a transparent support and three light sensitive silver halide emulsion layers, the two outer layers being predominantly sensitive to blue light, the middle layer being predominantly sensitive for another part of the spectrum, each of the outer layers being transmittant for the light rays for which the layer is predominantly sensitive, and at least one of the outer layers being insensitive to and being transmittant for light rays for which the middle layer is predominantly sensitive, the middle layer being colored yellow by a dyestuff which is not removable by ordinary photographic treating baths but which is selectively removable under the influence of the silver image, at least one of said outer layers and said yellow middle layer being basically of the same silver halide, so that they have substantially the same natural blue sensitivity range, said yellow middle layer having, before coloring, a speed of approximately  $\frac{1}{2}$  that of said last mentioned outer layer within said blue range, so that the light rays within said blue range which are necessary for sufficient and thorough exposure of said last mentioned outer layer are not capable of producing any appreciable light impression in said yellow middle layer.

7. A multilayer light sensitive material for color photography comprising a plurality of superposed silver halide emulsion layers predominantly sensitive to different parts of the spectrum, at least one silver halide emulsion layer being colored by a dyestuff which is not removable by ordinary photographic treating baths but which is selectively removable under the influence of a silver image and which transmits light rays to which the layer itself is predominantly sensitive, another of said layers superposed with respect to said colored layer being transmittant for and predominantly sensitive to light rays absorbed by said dyestuff but transmittant for and insensitive to light rays for which said colored layer is predominantly sensitive, said layers being basically of the same silver halide, so that they have substantially the same natural spectral sensitivity range, said colored layer having, before coloring, a speed so considerably lower than said superposed layer within said range, that the light rays within said range which are necessary for sufficient and thorough exposure of said superposed layers are not capable of producing any appreciable light impression in said colored layer, said colored layer being formed by an unripened emulsion and said superposed layer being formed by a ripened emulsion.

8. A light sensitive material for producing multi-color images comprising a transparent support and three light sensitive silver halide emulsion layers, the two outer layers being of the same predominant sensitivity, the middle layer being predominantly sensitive for another part of the spectrum, each of the outer layers being transmittant for the light rays for which the layer is predominantly sensitive, and at least one of the outer layers being insensitive to and being transmittant for light rays for which the middle layer is predominantly sensitive, the middle layer being colored yellow by a dyestuff which is not removable by ordinary photographic treating baths but which is selectively removable under the influence of the silver image, at least one of said outer layers and said yellow middle layer being basically of the same silver halide, so that they have substantially the same natural blue sensitivity range, said yellow middle layer having, before coloring, a speed so considerably lower than said last mentioned outer layer within said blue range, so that the light rays within said blue range which are necessary for sufficient and thorough exposure of said last mentioned outer layer are not capable of producing any appreciable light impression in said yellow middle layer.

9. A multi-layer light sensitive material for color photography comprising a plurality of superposed silver halide emulsion layers predominantly sensitive to different parts of the spectrum, at least one silver halide emulsion layer being colored yellow by a dyestuff which is not removable by ordinary photographic treating baths but which is selectively removable under the influence of a silver image and being predominantly sensitive to a spectral range other than blue, another of said layers superposed with respect to said colored layer being transmittant for and predominantly sensitive to blue light rays but transmittant for and insensitive to the spectral range for which said yellow layer is predominantly sensitive, said layers being basically of the same silver halide, so that they have substantially the same natural spectral sensitivity range, said colored layer having, before coloring, a speed so considerably lower than said superposed layer within said range, that the light rays within said range which are necessary for sufficient and thorough exposure of said superposed layers are not capable of producing any appreciable light impression in said colored layer, said colored layer being formed by an unripened emulsion and said superposed layer being formed by a ripened emulsion.

part of the spectrum, each of the outer layers being transmittant for the light rays for which the layer is predominantly sensitive, and at least one of the outer layers being insensitive to and being transmittant for light rays for which the middle layer is predominantly sensitive, the middle layer being colored by a dyestuff which is not removable by ordinary photographic treating baths but which is selectively removable under the influence of the silver image and which transmits light rays for which the layer itself is predominantly sensitive but absorbs light rays to which both the outer layers are predominantly sensitive, at least one of said outer layers and

5 said middle layer being basically of the same silver halide, so that they have substantially the same natural spectral sensitivity range, said colored middle layer having, before coloring, a speed so considerably lower than said last mentioned outer layer within said range, that the light rays within said range which are necessary for sufficient and thorough exposure of said last mentioned outer layer are not capable of producing any appreciable light impression in said colored middle layer, said middle layer being formed by an unripened emulsion and at least one of said outer layers being formed by a ripened emulsion.

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