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MULTILAYER MATERIAL FOR COLOR PHOTOGRAPHY AND METHOD OF MAKING THE SAME

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Fig. 1.

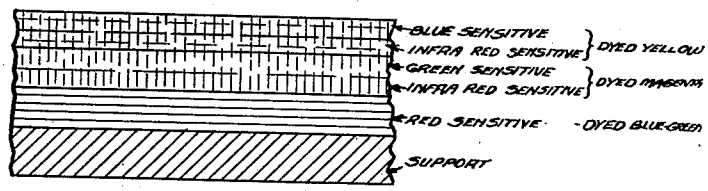


Fig. 2.

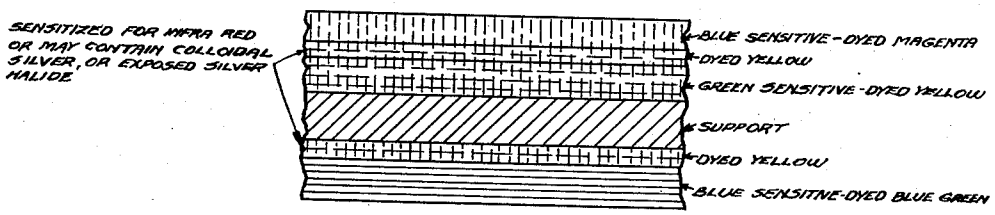
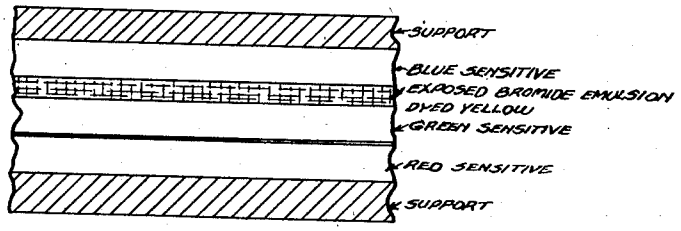


Fig. 3.



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MULTILAYER MATERIAL FOR COLOR PHOTOGRAPHY AND METHOD OF MAKING THE SAME

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7 Claims. (Cl. 95—2)

Multilayer light-sensitive materials are known in which at least one of the layers contains a dyestuff for forming the final image, which dyestuff acts simultaneously as a screening dye for subsequent layers which might be sensitive to light to which the superposed layer is to be exposed. The invention relates to materials of this kind and has for its object the provision of a material in which the amount and the distribution of the dyestuff is adapted to the desired screening effect on the one hand and to the requirements met with in the production of the multicolor image on the other hand. The invention is applicable in all cases in which the dyestuff quantity necessary for screening a layer sensitive to the same light which is used in the exposure of the preceding layer is in excess to that required in the most intensely colored parts of the final image.

According to the invention two adjacent layers of light-sensitive emulsion are used, both of which contain the image-forming dyestuff. This means that one layer in a multilayer material or several or all of them are replaced by a double layer one half of which contains the amount of dyestuff necessary for the coloration of the most intensely colored parts of the image and the other half layer of which contains such surplus of dyestuff as is required for preventing the light from penetrating into the layer which is to be screened by the dyestuff. The half of the layer which contains the surplus dyestuff is either sensitized for light rays which allow the individual and uniform exposure of this half or is fogged by a pre-treatment so that a uniform silver deposit will be obtained by developing. The layer may also contain exposed silver halide or colloidal silver which in the further treatment acts to decolorize this half of the layer and thus reduces the dyestuff concentration to the desired degree.

The position of the half of the layer intended to be decolorized and containing the surplus dyestuff may be above or below with respect to the other half intended to yield the dyestuff image, or two layers to be decolorized and containing the surplus dyestuff may be arranged on both sides of the layer which yields the dyestuff image. If the dyestuff in the colored layer is to screen the layer itself, as for instance the yellow image-forming dyestuff in a three layer material containing a blue sensitive front layer dyed magenta and a succeeding yellow dyed green sensitive layer, that half of the yellow layer which contains the surplus dyestuff faces the blue sensitive layer. In this case, this half of the yellow dyed emulsion may be sensitized to infra-red light and may be uniformly exposed to such light. If the third layer in the material is a blue sensitive layer which is to be exposed from the other side the yellow middle layer contains on both sides a yellow emulsion sensitized to infra-red. If on the other hand the dyestuff in the colored layer is to screen the following layer, as for instance a yellow dyestuff in a blue-sensitive layer arranged in front of one or more layers sensitized to green and red, but sensitive also to blue, that half of the yellow layer which contains the surplus dyestuff faces the following layers in the combined material. Thus, for example as shown in Fig. I of the drawing, the yellow dyed emulsion is applied in the form of two coatings on top of layers comprising a blue-green colored red-sensitive emulsion and a superposed double layer of magenta colored green-sensitive emulsion. After the first coating of yellow emulsion has been applied the composite material may be subjected to a weak illumination by blue light sufficient to expose the yellow emulsion but not the other two. After that, a second coating of yellow emulsion may be applied, the dyestuff concentration in this emulsion layer corresponding to the color intensity required at the most intensely colored parts of the image. The first coating may be specially sensitized for infra-red as shown, in which case it may be uniformly exposed to such light as heretofore explained. In the same manner the magenta dyed emulsion may be produced by the application of two coatings.

Instead of applying the entire layer by separately coating two part layers, the whole layer may be formed by a single coating process and there after different strata may be obtained within this single layer by a surface illumination during the manufacture of the layer or during the application thereof to the support. In order to render possible such exposure during the application a special sensitization, for instance to infra-red light, is given to the layer or layers.

As shown in Fig. II of the drawing a transparent support carries on the one side a yellow-dyed silver halide emulsion layer sensitized to green light, a yellow intermediate layer and a blue-sensitive magenta-colored layer on top thereof. The other side of the support carries first a yellow layer identical with the yellow intermediate layer cited above but coated directly on the support. Upon this yellow layer there is coated on the outer side a blue-sensitive emulsion of blue-green color.

The dyestuffs used are:

For the yellow emulsion: 0.6 g./sq.m. of Milling

Yellow G (Schultz Farbstofftabellen, 7th ed., vol. 1, No. 726).

For the two intermediate layers: 0.20 g./sq.m. of Milling Yellow G (Schultz Farbstofftabellen, 7th ed., vol. 1, No. 726).

For the magenta emulsion: 0.65 g./sq.m. of Polarbrillantred 3B (Brunner, Analyse der Azofarbstoffe, Springer/Berlin, 1929, page 110).

For the blue-green emulsion: 0.4 g./sq.m. of Direct Sky Blue (Schultz Farbstofftabellen, 7th ed., vol. 1, No. 513).

The intermediate layers either consist of a colored emulsion that has been exposed but not developed or of an unexposed emulsion that, however, contains cryptocyanine so that it may be uniformly exposed to infra-red light, or even of a colored gelatin solution of 2½% in which 6 g/L colloidal silver are evenly distributed.

The present invention is further applicable in cases in which the colored colloid layer acting as a light-filter is used in combination with a silver halide emulsion layer not carrying the same dyestuff as the filter layer or a dyestuff of similar properties. Filter layers containing a dyestuff which is resistant to ordinary photographic treating solutions but capable of being bleached in the presence of metallic silver and further containing means for uniformly decolorizing the layer under the influence of uniformly distributed silver, can be arranged in front of a light-sensitive layer which is colorless or colored and which may contain dyestuff-forming substances.

The means for decolorizing may consist of colloidal silver, of undeveloped silver halide which has been uniformly exposed or fogged or which can be uniformly illuminated owing to the presence of a sensitizer which renders the layer sensitive to light rays by which the layer can be illuminated without exposure of the differently sensitized layers. After the exposure of the material and after the production of latent images in the different layers and after the production of the metallic silver images the material having silver pictures in the image-bearing layers and a uniform silver deposit in the intermediate layer is treated with a dye-destroying solution such as a 5 per cent hydrobromic acid or the solution of 3 per cent thiocarbamide and 1 per cent sulphuric acid which destroys the dyestuff in the filter layer in uniform manner. Thus, for example, as shown in Fig. III of the drawing, the front element of a bi-pack has a blue sensitive layer, and a green sensitive layer coated on the same side of a transparent support with the blue sensitive silver halide layer next to the support and with the interposition of an intermediate gelatin layer which contains the dyestuff Milling Yellow G, 0.5 g. per sq. m. (Schultz Farbstofftabellen, 7th ed., volume 1, No. 726) and an amount of exposed sliver bromide emulsion, the quantity of which can be determined by an experiment and which is in an excess to the amount required for decolorizing the layer when treated for about three minutes with a 5 per cent solution of hydrobromic acid. The rear film of the bi-pack carries an ordinary red-sensitive film. The bi-pack is exposed through the support of the front element, developed and fixed. Thereafter, the front element is dyed by soaking it in a blue dyestuff solution, for example, a 1% solution of Pontamine Sky Blue which uniformly dyes all of the layers. The dyestuff is thereafter destroyed at the places of the silver deposit by treating with an acid thiocarbamide solution or with hydrobromic acid, so that two blue colored images are obtained in the light-sensitive layers whereas the dyestuff is destroyed totally in the filter-layer. The remnant silver is bleached with a bleacher containing potassium bichromate for example one of the following formula:

Potassium ferricyanide	grams	37.5
Potassium bromide	do	56.25
Potassium dichromate	do	37.5
Acetic acid	ccs	10
Water	ccs	2000
Potassium alum, 5 per cent solution	ccs	1000

The bleacher simultaneously acts to tan the gelatin. The film is fixed with hypo and dried and thereafter treated with a 3 per cent sodium hydrosulphite solution which acts to decolorize the blue dyestuff image at the unhardened points of the upper layer but which is prevented from reaching the second light-sensitive layer by the uniformly hardened gelatin of the middle layer. The decolorized outer layer still contains the tanned relief corresponding to the original silver image and the unhardened places can be colored by a water soluble dyestuff.

What is claimed is:

1. A light-sensitive multilayer material for color photographic purposes comprising several silver halide emulsion layers equal in number to the number of color selection pictures to be recorded in the material each being predominantly sensitized to a predetermined spectral range for recording therein a color selection picture and an additional layer of colored colloid in front of one of said silver halide emulsion layers, said additional colloid layer being uniformly dyed with a dyestuff which is resistant to ordinary photographic treating solutions but capable of being bleached with the aid of metallic silver and which absorbs a spectral band for which said one of said silver halide emulsion layers is sensitive, but transmits light of a different spectral region for which said one of said silver halide layers is predominantly sensitized, said additional colloid layer further comprising an evenly distributed substance which is capable of assisting in the uniform bleaching of the dye by dye-destroying agents, said substance being selected from the group of substances which consists of finely distributed silver, colloidal silver, fogged silver halide emulsion, exposed silved halide and color sensitized silver halide sensitized differently from the predominant sensitivities of said first mentioned silver halide emulsion layers.

2. A light-sensitive multilayer material for color photographic purposes comprising several silver halide emulsion layers equal in number to the number of color selection pictures to be recorded in the material each being predominantly sensitized to a predetermined spectral range for recording therein a color selection picture at least one of the silver halide emulsion layers being dyed with a dye for the formation of the final image to the color intensity required at the most intensely colored parts of the final image, the dye being resistant to ordinary photographic treating solutions but capable of being bleached with the aid of metallic silver, an additional colloid layer adjacent to the colored silver halide layer being uniformly dyed with substantially the same dyestuff, the additional colloid layer further comprising an evenly distributed substance which is capable of assisting in the uniform bleaching of the dye by dye-destroying agents, said substance being selected from the group of substances, which consists of finely distributed

silver, colloidal silver, fogged silver halide emulsion, exposed silver halide and color sensitized silver halide sensitized differently from the predominant sensitivities of said first mentioned silver halide emulsion layers.

3. A light-sensitive multilayer material for color photographic purposes comprising several silver halide emulsion layers equal in number to the number of color selection pictures to be recorded in the material each being predominantly sensitized to a predetermined spectral range for recording therein a color selection picture, at least one of the silver halide emulsion layers being dyed with a dye for the formation of the final image to the color intensity required at the most intensely colored parts of the final image, the dye being resistant to ordinary photographic treating solutions but capable of being bleached with the aid of metallic silver, an additional colloid layer adjacent to each side of the colored silver halide layer being uniformly dyed with substantially the same dyestuff, the additional colloid layers further comprising an evenly distributed substance which is capable of assisting in the uniform bleaching of the dye by dye-destroying agents, said substance being selected from the group of substances, which consists of finely distributed silver, colloidal silver, fogged silver halide emulsion, exposed silver halide and color sensitized silver halide sensitized differently from the predominant sensitivities of said first mentioned silver halide emulsion layers.

4. A light-sensitive multilayer material for color photographic purposes comprising several silver halide emulsion layers equal in number to the number of color selection pictures to be recorded in the material each being predominantly sensitized to a predetermined spectral range for recording therein a color selection picture, and an additional layer of colored colloid positioned between two of said sliver halide emulsion layers, said additional colloidal layer being uniformly dyed with a dyestuff which is resistant to ordinary photographic treating solutions but capable of being bleached with the aid of metallic silver and which absorbs a spectral band for which one of said two silver halide emulsion layers is sensitive, but transmits light of a different spectral region for which said one of said two silver halide emulsion layers is predominantly sensitized, said additional colloidal layer further comprising an evenly distributed substance which is capable of assisting in the uniform bleaching of the dye by dye-destroying agents, said substance being selected from the group of substances which consists of finely distributed silver, colloidal silver, fogged silver halide emulsion, exposed silver halide and color sensitized silver halide sensitized differently from the predominant sensitivities of said first mentioned silver halide emulsion layers.

5. A process of producing a colored filter layer in a multilayer photographic material for multicolor photography which comprises, forming a silver halide emulsion layer which is sensitive to a predetermined spectral range, coloring a silver halide emulsion which is sensitive to a range different from said predetermined spectral range and which is used for the production of the filter layer with a dye which is resistant to ordinary photographic treating solutions but capable of being bleached with the aid of metallic silver, forming a filter layer of said last mentioned emulsion which is superposed with respect to said first mentioned emulsion layer, and uniformly illuminating the said filter layer with light to which it is sensitive and to which said first mentioned emulsion layer is not sensitive to completely expose said filter layer and form therein a diffuse distribution of exposed silver halide.

6. A process of producing a colored filter layer in a multilayer photographic material for multicolor photography which comprises, forming a silver halide emulsion layer which is sensitive to a predetermined spectral range, coloring a silver halide emulsion which is sensitive to a range different from said predetermined spectral range and which is used for the production of the filter layer with a dye which is resistant to ordinary photographic treating solutions but capable of being bleached with the aid of metallic silver, forming a filter layer of said last mentioned emulsion which is superposed with respect to said first mentioned emulsion layer, uniformly illuminating the said filter layer with light to which it is sensitive and to which said first mentioned emulsion layer is not sensitive to completely expose said filter layer and form therein a diffuse distribution of exposed silver halide, and forming another superposed silver halide emulsion layer which is dyed with substantially the same dye as said filter layer.

7. A process of producing a colored filter layer in a multilayer photographic material for multicolor photography which comprises, coloring a silver halide emulsion which is sensitive to a predetermined spectral range, forming a layer of said emulsion, coloring a silver halide emulsion which is sensitive to a range different from said predetermined spectral range and which is used for the production of the filter layer with a dye of substantially the same color as said first mentioned emulsion layer, said dye being resistant to ordinary photographic treating solutions but capable of being bleached with the aid of metallic silver, forming a filter layer of said last mentioned emulsion which is superposed with respect to said first mentioned emulsion layer and uniformly illuminating the said filter layer with light to which it is sensitive and to which said first mentioned emulsion layer is not sensitive to completely expose said filter layer and form therein a diffuse distribution of exposed silver halide.

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