April 20, 1943. W. MICHAELIS 2,316,803

PHOTOGRAPHIC MATERIAL FOR TAKING COLOR PHOTOGRAPHS

Filed Dec. 23, 1939

Fig. 1.

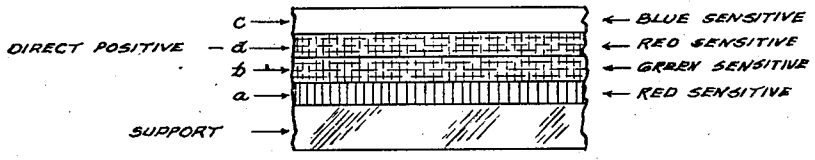


Fig. 2.

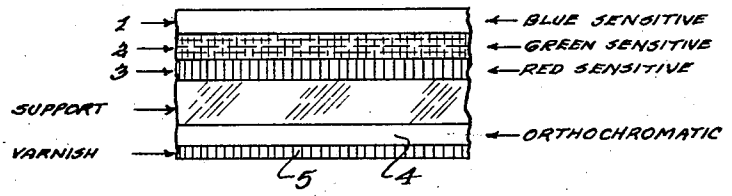
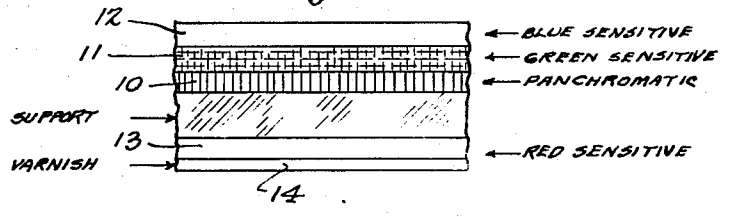


Fig. 3.



Inventor

Walter Michaelis

By F. Gerald Toye

Attorney

Patented Apr. 20, 1943 2,316,803

UNITED STATES PATENT OFFICE

2,316,803

PHOTOGRAPHIC MATERIAL FOR TAKING COLOR PHOTOGRAPHS

Walter Michaelis, Brussels-Forest, Belgium, assignor, by mesne assignments, to Chromogen, Incorporated, a corporation of Nevada

Application December 23, 1939, Serial No. 310,847
In Great Britain December 28, 1938

10 Claims. (Cl. 95—2)

The present invention relates to the field of color photography and more particularly to masking methods of the same general kind as described in my prior Patents No. 2,136,143, dated November 8, 1938; No. 2,193,931, dated Mar. 19, 1940, and No. 2,241,413, dated May 13, 1941.

The subject of the present invention is a process for producing multicolor images and a multilayer light-sensitive material which is especially suitable for carrying out the process. The invention is especially useful for taking color photographs in a multilayer material and for producing a multicolor image therein. The color pictures thus produced are to be used as printing prototypes, and accordingly the material comprises at least two silver halide layers that are differently sensitized for the separate recording of various color values of the object photographed. Colored part-images are produced in the multilayer material from the color selections recorded in each of the layers, the dyes used for the formation of the part-images being so selected that exposure to sources of printing light of different colors yields a print of either one or the other of the part-images recorded in the multilayer material.

The expression "printing prototype" used herein is intended to connote any image from which a print is taken in a photographic printing process in which the same is disposed between the source of printing light and the printing layer whether said image be a black and white, monochrome or multicolor image and whether the same is an original or not.

It is recognized that it is difficult to find two dyes that are of such a nature that the light rays strongly absorbed by one are practically completely transmitted by the other. This condition must, however, be fulfilled if, while printing one colored part-image, it is sought to avoid the undesired extraneous printing of one or more of the differently colored part-images. For instance, when a yellow-dyed part-image representing any color selection has to be printed with blue light, and when there is present a magenta-dyed part-image representing any other color selection, the result of the absorption of blue light usually met with in the case of magenta dyes is that the print produced by exposure to blue light will reproduce not only the part-image recorded in yellow, but it will be falsified by an undesired printing effect of the part-image recorded in magenta dye.

The object of the present invention is to make allowance in advance for this troublesome factor in printing from multicolor matrices by providing already at the time of taking the negative means of compensating for the shortcomings later arising in the printing process; this is effected by the inclusion of a special layer in the multilayer taking material.

According to the present invention a taking material is used which comprises a plurality of light-sensitive layers which are inseparable by mechanical means and which are united on a common transparent support. The layers are sensitized for light of different fundamental colors in accordance with the usual principles of color photography. In the different layers differently colored part-images are subsequently produced from the color selections photographically recorded by the exposure. In addition to these ordinary emulsion layers usual in multicolor photographic processes, the material according to the invention, contains an additional silver halide emulsion layer. This latter layer is used for the production of a supplementary colored image. The color of this supplementary image is similar to or preferably the same as the color of that colored part-image, the print of which, owing to the interference of a differently colored record representing a different fundamental color, cannot be obtained free of an extraneous image.

The additional layer can be arranged in different ways and can be formed of light-sensitive emulsions of various kinds. This layer as well as the other layers may be uncolored or may contain, already prior to the exposure, the dye used for the formation of the image or a dye-forming substance from which the dye can be obtained. Preferably the front layer of the multilayer material is either colorless or of a weak yellow color. It should be borne in mind that the colored image to be produced in the additional layer is to be a reversed image as compared with the colored part-image to be masked out in the printing process and that either the additional emulsion layer itself or its treatment is adapted to the formation of such a reversed image.

In practicing the invention, use may be made, for example, of an emulsion which upon ordinary development yields a positive silver image, this emulsion being used for the formation of a light-sensitive layer in addition to the normal emulsion layers of the multilayer taking materials; or an ordinary emulsion may be used for the additional layer and employed for producing a colored negative, while the color selections recorded in the other layers, or at least that which interferes

with another dye-image during the printing are transformed into colored positives or vice versa. Various methods of producing such images are described in the following examples and the materials used therein are illustrated in the accompanying drawing of which Fig. 1 is a diagrammatic cross sectional representation of a light sensitive material suitable for use in practicing the process described in Example 1; Fig. 2 is a similar representation of an alternative light sensitive material such as described in Example 2; and Fig. 3 is also a similar representative of an alternative light sensitive material such as described in Example 3.

Example 1.—As shown in Fig. 1, a transparent support has first coated on to it a red-sensitive emulsion layer *a* colored with the dye Benzopurpurine 10 B (Schultz Farbstofftabellen, Leipzig 1931, 7th ed., vol. 1, No. 489) in a concentration of 1 gram per sq. m. surface. Superposed on layer *a*, there is a green-sensitive layer *b* dyed yellow with 1 gram Chrysophenine G (Schultz l. c., No. 726) per sq. m. Interposed between layer *b* and an ordinary blue-sensitive emulsion front layer *c* there is a supplementary layer *d*. Layer *d* is formed of an emulsion that yields a positive silver image direct upon ordinary development. It is also colored with the dye Chrysophenine G (Schultz l. c., No. 726) in a concentration of 0.3 grm. per sq. m. and is predominantly red-sensitive. Layer *c* may be coated immediately upon layer *d*, or it may be on a separate support so that the whole material forms a bi-pack, the front part of which comprises a support and layer *c* while the rear part comprises a support and the negative layers *a* and *b* and the direct positive layer *d*. Upon exposure, latent silver images are formed in each layer and when developed, layers *a*, *b* and *c* produce negative silver pictures, whereas a positive silver picture is produced in layer *d*. The silver pictures in the dyed layers are converted into dye-pictures by treatment in a bath, containing e. g. a 5% solution of thiocarbamide with the addition of 1% sulphuric acid which locally destroys the dye at the places where silver is present. The colorless layer *c* is either converted by any of the known processes into a dye-picture, or if it is on a separate support the silver picture itself may be used in the usual manner. The multicolored picture obtained in layers *a*, *b* and *c* comprises the following components:

(1) a magenta-dyed positive part-image representing the red color selection in layer *a*, (2) in layer *b* a yellow-dyed positive part-image representing the green color selection of the object, and (3) in layer *d* a second part-image representing the red color selection of the object, but yellow-dyed and negative. This multicolor photograph serves as a matrix for printing either in successive separate printing operations or simultaneously in a single printing step, whereby the magenta-colored part-image is printed into a green-sensitive layer with green light and the yellow-colored part-image into a blue-sensitive layer with blue light, the two printing layers being either superposed on a common support or on separate supports. In printing with green light it is only the magenta-colored part-image that serves as a matrix, for the layers *b* and *d* transmit practically as much green light as the yellow areas as at the areas where no dye is present. On the other hand, when blue light is employed for printing, the yellow dye acts as the principal absorbent of the light, although the magenta dye in layer *b* also functions in the same manner to a certain extent. When printing with blue light, a print is therefore obtained that for the sake of simplicity may be regarded as a composite print which reproduces the yellow part-image in layer *b*, but comprises also both a negative print resulting from the magenta part-image in layer *a* and a positive print resulting from the yellow part-image in layer *d*. Now as both layer *a* and layer *d* were originally exposed by red light, the part-images recorded therein represent the same color selection and are identical, except for the fact that they are negative and positive records respectively. The prints obtainable from these images, which are mutually reversed, complement each other and the actual print records substantially nothing but the print from the yellow part-image of layer *b*. In order to assure a maximum of the mutual neutralization effect of the picture in layers *a* and *d*, it is expedient that the yellow dye in layer *d* is present in such a maximum concentration as to exhibit for the blue printing light the same absorption as the magenta dye; or that at least the maximum density difference for blue light is approximately as great in the yellow dye-image in layer *d* as in the magenta dye-image in layer *a*.

As the spectral composition of the blue printing light may be varied within rather wide limits, it is much simpler to effect the correction by varying the printing light than by attempting a precise adjustment of the emulsion. The most suitable printing light can be selected by determining the absorption curve of both the magenta dye in layer *a* and the yellow dye in layer *d* at the points where these dyes are present in their maximal concentration, determining the intersection of these curves and using a printing light of approximately the wave length corresponding to the point of intersection.

The above example is but one illustration of the application of the invention. More than one direct-positive emulsion layer may be employed, e. g. a layer of this nature may be interposed also between the yellow and the magenta colored negative emulsion layers. The invention may also be practiced with other taking materials where the multicolor picture is not produced by dye-destruction but for example by local dye-synthesis or local coloring. The supplementary layer here referred to as layer *d* may also be in another position than that described in the example.

Example 2.—As shown in Fig. 2, a three-layer taking material, comprising a colorless front layer 1 of the same kind as layer *c* in Example 1; a yellow-dyed green-sensitive layer 2 the same as layer *b* in Example 1; and a magenta-dyed red-sensitive layer 3 the same as layer *a* in Example 1, all of these layers superposed on one side of a transparent support, has on the opposite side of the support a silver halide orthochromatic light-sensitive layer 4. The latter layer is backed with a layer 5 of varnish soluble in alcohol and preferably dyed red.

The material is exposed in the camera with the triple-coated side nearest the lens. The exposure results in three latent images, while the back layer 4 remains unexposed owing to the screening effect of the yellow and magenta dyes in layers 2 and 3. The film is developed and fixed as usual and the colorless front layer 1 is dyed blue-green, e. g. with Pontamine Sky Blue 5 BX (Schultz l. c., No. 513). The dyes in layers 2 and 3 are locally destroyed by an acid thiocarbamide

solution and the remaining silver in the material is bleached in a red, green or yellow darkroom light with an acid cupric chloride solution and fixed out under the same conditions. A three-colored positive is thus obtained in the triple-coated side. Now the material is exposed to green light, if the preceding steps have not been carried out in green or yellow light. This exposure to green light or the carrying out of the preceding steps in green darkroom illumination yields a latent image in the supplementary layer 4 behind the support, this latent image reproducing those portions of the magenta layer 3 that have been decolorised and rendered transparent for green light by the dye destruction. The varnish layer 5 covering the supplementary layer 4 is now removed or dissolved by an organic solvent and the whole film is introduced into a developer that yields a negative silver image in the supplementary layer 4. The developer used may be of the kind that yields a yellow dye in situ with the silver so that a yellow negative will be obtained in the supplementary layer 4 after the removal of the silver image by Farmer's reducer. Or, alternatively, the silver image in the supplementary layer 4 may be transformed into a mordant and dyed with a yellow dye.

Example 3.—The taking material illustrated in Fig. 3 comprises three layers coated on one side of a transparent support, viz: a panchromatic emulsion layer 10 dyed with Benzopurpurine 10 B immediately on the support; superposed on this a green-sensitive emulsion layer 11 dyed with Chrysophenine G; and a colorless blue-sensitive outer layer 12. The opposite side of the support is coated with a red-sensitive colorless emulsion layer 13, the sensitivity of which is considerably less than that of the red-sensitive layer on the other side. This red-sensitive layer on the back of the support is sealed with a coating 14 of varnish soluble in organic solvents.

The multilayer material is exposed in a camera with the three layers 10, 11 and 12 nearest the lens and latent color selection images are thus obtained in these three layers on one side of the support, while the layer 13 behind the support is not affected. The latent images are developed and fixed and thereafter the material is exposed from the three-layer side to a strong red light. In the red-sensitive layer 13 behind the support there is thus obtained a latent image that represents a combined print of the three silver images in the front layers. Thereupon the colorless outer layer 12 in front of the material is uniformly colored with a blue-green dye and the whole material immersed in an acid thiocarbamide bath that locally bleaches the dyes in the three front layers. The varnish coating 14 on the back of the support is then dissolved and the material developed again, a silver image thus being obtained in the supplementary back layer 13. The material is then treated in a tanning-bleaching bath that converts the silver into a soluble silver salt and simultaneously hardens the gelatin where silver is present. The material is then fixed and thereafter the layer 13 on the back of the support is treated with a yellow dye that colors the places of this layer that are not hardened.

The coloring of the rear layer 13 must be comparatively weak, for the picture therein is a reproduction of every color selection picture recorded separately in the three layers on the other side of the support. Accordingly, its intensity should be only of such a degree that when exposed to blue printing light it compensates the magenta dyed and the bluegreen dyed color selection images but does not cancel the yellow dyed color selection image. The following example illustrates the phenomena to be taken into consideration with regard to the intensity of the supplementary dye image.

Example 4.—The material comprises the three layers mentioned in the preceding example, all being on the same side of the support. No supplementary layer is required in this method of practicing the invention. The material is exposed in the camera, the silver images developed and fixed. The outermost colorless layer is uniformly dyed bluegreen and the dye in the three layers then locally destroyed by treatment in an acid thiocarbamide bath. The silver images are then bleached out with an acid cupric chloride solution and the film then exposed to a strong light so that the silver images are capable of being redeveloped. The material is then treated a second time with a developer that yields a yellow dye in situ with the silver. The silver images are then bleached with Farmer's reducer.

The process described above results in a film that contains in each of the layers a different positive color selection record, each of which is supplemented by a negative yellow-dyed part-image. It is obvious that the negative yellow part-image must not be of the same maximum density as the yellow positive part-image, for in that case the two images would cancel each other completely and no print would be obtained from the yellow-dyed positive. If the maximum density of the yellow negative is only but about half of the maximum density of the yellow positive the result is only a flattening of the yellow positive. The yellow-dyed negatives in the other layers are also comparatively weak, and they should be of the same absorption for blue printing light at the parts most intensely dyed as the bluegreen or the magenta dye at the most intensely colored areas are for blue printing light. The second development yielding the supplementary yellow negative images may be restricted to one or the other outer layer, so that there is no yellow negative formed in the middle layer. To this end the film is exposed from the front and rear to a weak light, preferably ultraviolet light, before the second development and thus only the silver salt in the outermost and innermost layers is capable of being redeveloped.

A supplementary dye-image may also be obtained in another manner than as described above, for example the second color development may be employed in cases where the previously formed dye-image is not produced by dye destruction. For instance, the first as well as the second image may be obtained by color development, the silver halide not being fixed out after the first color development but employed for the second colored development.

What is claimed is:

1. The process of producing a multicolor image on a light-sensitive photographic multilayer film having a transparent support and at least three light-sensitive silver halide emulsion layers inseparably united with said support, two of said layers being sensitized to record light rays of substantially the same color and the third layer being sensitized to record differently colored light, which comprises exposing simultaneously the said three layers to a multicolored object illuminated with composite light to thereby record latent images in all of the light-sensitive layers,

converting the latent images within said first mentioned two layers into dye images of opposite density gradation and of different colors having partly overlapping absorption, converting the latent image within said third layer into a dye image of a color which is highly transparent for light for which only one of the other images is strongly absorbent and which is strongly absorbent for light of a spectral region in which the absorptions of the two other images overlap each other.

2. The process of producing a multicolor image on a light-sensitive photographic multilayer film having a transparent support and at least three light-sensitive silver halide emulsion layers inseparably united with said support, two of said layers being sensitized to record light rays of substantially the same color and the third layer being sensitized to record differently colored light, which comprises exposing simultaneously the said three layers to a multicolored object illuminated with composite light to thereby record latent images in all of the light-sensitive layers, converting the latent images within said first mentioned two layers into dye images of opposite density gradation and of different colors having partly overlapping absorption, converting the latent image within said third layer into a dye image of a color which is highly transparent for light for which only one of the other images is strongly absorbent and which is strongly absorbent for light for which the absorptions of the two other images at their most intensely colored points are equal to each other.

3. The process of producing a multicolor image on a light-sensitive photographic multilayer film having a transparent support and at least three light-sensitive silver halide emulsion layers inseparably united with said support, two of said layers being sensitized to record light of substantially the same color and the third layer being sensitized to record differently colored light, which comprises exposing simultaneously the said three layers to a multicolored object illuminated with composite light to thereby record latent images in all of the light-sensitive layers, developing the latent images to form silver images and converting the silver images within said first mentioned two layers into dye images of opposite density gradation and of different colors having partly overlapping absorption, converting the silver image within said third layer into a dye image of a color which is highly transparent for light for which only one of the other images is strongly absorbent and which is strongly absorbent for light of a spectral region in which the absorptions of the two other images overlap each other.

4. The process of producing a multicolor image on a light-sensitive photographic multilayer film having a transparent support and at least three light-sensitive silver halide emulsion layers inseparably united with said support, two of said layers being formed by emulsions which after exposure and development yield silves images of opposite character and which are sensitized to record light rays of substantially the same color and the third layer being sensitized to record differently colored light, which comprises exposing simultaneously the said three layers to a multicolored object illuminated with composite light to thereby record latent images in all of the light-sensitive layers, developing the latent images to form silver images and converting the silver images within said first mentioned two layers into dye images of opposite density gradation and of different colors having partly overlapping absorption, converting the latent image within said third layer into a dye image of a color which is highly transparent for light for which only one of the other images is strongly absorbent and which is strongly absorbent for light of a spectral region in which the absorptions of the two other images overlap each other.

5. The process of producing a multicolor image on a light-sensitive photographic multilayer film having a transparent support and at least three light-sensitive layers inseparably united with said support, at least two of said layers being sensitized to record different colors and the number of light-sensitive layers being in excess to the number of color separations which are to be recorded on the film, which comprises recording the color separations by a single exposure in the multilayer film, forming within two of said layers dye images of opposite density gradation and of different colors having partly overlapping absorption and representing the same color separation of the object, forming within a third layer a dye image representing another color separation of the object and being of a color which is highly transparent for light for which only one of the opposite density gradation images formed in said two layers is strongly absorbent and which is strongly absorbent for light of a spectral region in which the absorptions of the two other images overlap each other.

6. The process of producing a multicolor image from a light-sensitive photographic multilayer film having a transparent support, at least three light-sensitive silver halide emulsion layers inseparably united with said support and coincident latent images in the said three layers, the latent images in two of said layers representing identical color values of the photographed object and the latent image in the third layer representing another color value of the same object, which comprises converting the latent images within said first two layers into dye images of opposite density gradation and of different colors having partly overlapping absorption, converting the latent image within said third layer into a dye image of a color which is highly transparent for light for which only one of the opposite density gradation images formed in said two layers is strongly absorbent and which is strongly absorbent for light for which the absorptions of the two other images at their most intensely colored points are equal to each other.

7. A light-sensitive multilayer film comprising a support, a plurality of superposed differently sensitized silver halide emulsion layers for recording the various desired color separations of a multicolor image, each of said layers being selectively sensitive for light for which the preceding layers are transmittant and being formed by an emulsion, the exposed portions of which are more developable than the unexposed portions, and an additional layer selectively sensitive for a part only of the light for which said other layers are sensitive, said light being light for which the preceding layers are transmittant, and said additional layer being formed by an emulsion the unexposed portions of which are more developable than the exposed portions.

8. A light-sensitive multilayer film comprising a support, a plurality of superposed differently sensitized silver halide emulsion layers for recording the various desired color separations

of a multicolor image, each of said layers being selectively sensitive for light for which the preceding layers are transmittant and being formed by an emulsion, the exposed portions of which are more developable than the unexposed portions, and an additional layer selectively sensitive for a part only of the light for which said other layers are sensitive, said light being light for which the preceding layers are transmittant, and said additional layer being formed by an emulsion the unexposed portions of which are more developable than the exposed portions, at least one of the light-sensitive layers comprising a substance for the production of a dye image.

9. A light-sensitive multilayer film comprising a support and a plurality of superposed differently sensitized silver halide emulsion layers for recording the various desired color separations of a multicolor image, each of said layers being selectively sensitive for light for which the preceding layers are transmittant, and an additional light-sensitive layer, said layer being sensitive to a part only of the light for which said other layers are sensitive, one of said plurality of layers being colored with a dyestuff which is highly transparent for light strongly absorbed by a dyestuff used in coloring another of said plurality of layers and strongly absorbent for light absorbed to a lesser extent by said dyestuff used in coloring said other of said plurality of layers, said additional layer being colored with a dyestuff which is strongly absorbent for light of a spectral region in which the absorptions of said first mentioned dyestuffs overlap each other, said plurality of layers being formed of an emulsion the exposed portions of which are more developable than the unexposed portions, and said additional emulsion being formed of an emulsion the unexposed portions of which are more developable than the exposed portions.

10. A light-sensitive multilayer film comprising a support and a plurality of superposed differently sensitized silver halide emulsion layers for recording the various desired color separations of a multicolor image, each of said layers being selectively sensitive for light for which the preceding layers are transmittant, and an additional light-sensitive layer, said layer being sensitive to a part only of the light for which said other layers are sensitive, one of said plurality of layers comprising a substance for the production of a dye which is highly transparent for light strongly absorbed by a dyestuff used in coloring another of said plurality of layers and strongly absorbent for light absorbed to a lesser extent by said dyestuff used in coloring said other of said plurality of layers, said additional layer comprising a substance for the production of a dyestuff which is strongly absorbent for light of a spectral region in which the absorptions of said first mentioned dyestuffs overlap each other, said plurality of layers being formed of an emulsion the exposed portions of which are more developable than the unexposed portions, and said additional emulsion being formed of an emulsion the unexposed portions of which are more developable than the exposed portions.

WALTER MICHAELIS.