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PROCESS OF PRODUCING MULTICOLOR IMAGES

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The present application is in part a continuation of my co-pending application Ser. No. 243,886 filed December 3, 1938 and subject matter claimed herein has been described in said prior application.

The invention relates to the production of multicolor pictures in a multilayer photographic material, by processes in which colored part pictures representing the various color separations are obtained successively in different layers through the effect of various treating baths. In processes of this kind it is necessary to restrict to certain layers the action of the treating baths employed to produce differently colored images. In order to restrict the effect of the bath to the layer or layers it is destined to affect, there are provided intermediate layers between the layers in which the part-images are recorded, and these intermediate layers are hardened or tanned after one layer has received its final color and before another layer is finally colored. By means of special composition or sensitizing, the intermediate layers of the original multilayer material are rendered capable of being selectively hardened in the course of the process of obtaining the multicolor image. To this end there are employed either a number of intermediate layers that are differentially sensitized for various ranges of infrared light, or one of the intermediate layers is sensitized for infrared light whilst the other intermediate layer is formed by a uniformly exposed or fogged silver halide emulsion.

Example 1.—A bipack exposure material is used the front element of which 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 dye Milling Yellow G (Schultz Farbstofftabellen, Leipzig 1931, 7th ed., vol. 1, No. 726), 0.5 grm. per sq. m., and an amount of exposed silver bromide emulsion, the quantity of which can be determined by an experiment and which is in an excess to the amount required for decolorising the layer when treated for about three minutes with a 5 per cent solution of hydrobromic acid. The rear film of the bipack carries an ordinary red-sensitive film. The bipack is exposed through the support of the front element, developed and fixed. Thereafter, the front element is dyed by soaking it in a blue dye solution, for example, a 1% solution of Pontamine Sky Blue 6B (Schultz l. c., No. 510) which uniformly dyes all of the layers. The dye 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 dye 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	g—	37.5
Potassium bromide	g—	56.25
Potassium dichromate	g—	37.5
Acetic acid	cc—	10
Water	cc—	2000
Potassium alum, 5% solution	cc—	1000

The bleacher simultaneously acts to tan the gelatin. The film is fixed with hypo and dried and thereafter treated with a 3% sodium hydrosulphite solution which acts to decolorise the blue dye 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 decolorised outer layer still contains the tanned relief corresponding to the original silver image and the unhardened places can be colored by a water soluble dye.

Example 2.—The multilayer material exposed to the object comprises three silver halide emulsion layers for the production of color separation images, one layer being sensitized for blue, the others for green and red respectively. The blue-sensitive layer forms the surface layer of the multilayer material and the front layer for the exposure; between this layer and the next there is an intermediate emulsion layer containing a yellow screening dye and finely divided silver halide that has been exposed. Between the green-sensitive middle layer and the red-sensitive rear layer which is next to the common support there is a gelatin layer containing silver halide that is sensitive to infrared light. The latter layer may, if desired, contain a red dye. Alternatively, the middle layer might be sensitized for red and the rear layer for green without a filter dye in the layer between. The exposure to the object is effected in a camera, infrared light being excluded.

The exposed film is developed but not fixed, the result being that black silver images are obtained in the three layers sensitized for blue, green and red respectively while the pre-exposed intermediate layer shows a uniform blackening. The whole film is colored with a dye, the color of which depends on the color to be given to the

color selection record in the rear layer. If this layer was sensitized for red light and if it is desired to produce a positive in the correct colours the whole film is dyed blue-green for example by Brillant Benzo Fast Green GL (Brillantbenzoethtgrün GL, Schultz Farbstofftabellen, Leipzig 1939, 7th ed., Supplement II, page 131), and if the rear layer was sensitized for green light the whole film is dyed magenta, for example by Diamin Fast Pink B (Diaminechtrosa B, Schultz Farbstofftabellen, Leipzig 1932, 7th ed., vol. 2, page 69) or Benzopurpurine 10B (Schultz Farbstofftabellen, Leipzig 1931, 7th ed., vol 1, No. 489). The whole film is then exposed to intense infrared light and subsequently developed in a tanning developer, such as a pyrocatechin developer without sulphite that simultaneously hardens and blackens the infrared-sensitive intermediate layer. The whole film is then fixed and then immersed in an aqueous solution containing about 3% sodium hydrosulphite which destroys the dye in the outer layers but which is prevented from penetrating into the rear layer by the hardened intermediate layer; the treatment may thus easily be determined as soon as the outer layers have become colorless. These decolorized layers are then permeated with a different dye, either by immersion in a bath of magenta, such as Tuchechtbrillantrot 2B (Schultz Farbstofftabellen, Leipzig 1932, 7th ed., vol. 2, page 221) or of bluegreen dye, such as Pontamine Sky Blue 5BX (Schultz Farbstofftabellen, Leipzig 1931, 7th ed., vol. 1, No. 513) according to whether the rear layer was dyed bluegreen or magenta. The hardened intermediate layer here also prevents the penetration of the dye into the rear layer already dyed and the process of dyeing is terminated as soon as the outer layers are uniformly colored. The dyes in all layers are then locally destroyed at the areas where silver is present by treatment with an acid thiocarbamide solution or with a diluted solution of hydrobromic acid, e. g. a solution of 5% hydrobromic acid with a content of 0.01% 2-oxy-3-aminophenazine. The treatment is continued until the dye-destroying solution has penetrated through the hardened intermediate layer and the dye has been locally destroyed in the rear layer as well as in the outer layers. In view of the delayed action of the dye-destroying solution in the rear layer, it is to be recommended that the dye employed for coloring this layer be of such a nature that it is easier bleached out than the dye used for coloring the outer layers, or there may be a catalyst incorporated in the emulsion employed for the rear layer before it is coated on the support, so that the destruction of the dye in this layer is accelerated. A catalyst of this kind is 3,3'-carbonyl-bis-[2-oxy-3-aminophenzanine]. The silver still present is converted into a silver salt that may be fixed out and for this purpose a tanning bleacher is employed, e. g.

Potassium ferricyanide	g--	37.5
Potassium bromide	g--	56.2
Potassium bichromate	g--	37.5
Acetic acid	cc--	10
5% solution of potassium alum	cc--	1000
Water	cc--	2000

This bleaching bath hardens the gelatin at the same time, so that the uniform silver deposit present in the intermediate layer between the front emulsion layer and the middle layer leads to a uniform hardening of this intermediate layer. The whole film is fixed with a fixing solution, dried and treated with a 3% aqueous solution of sodium hydrosulphite. This destroys the dye at the areas in the surface layer that have not been hardened, but is prevented by the uniformly tanned intermediate layer from penetrating into the middle layer and thus destroying the dye therein. The decolorized surface layer contains a mordanted relief that is capable of absorbing dye solutions at the areas not affected by light and these areas are dyed by immersion in a yellow dye solution, such as a solution of Chrysophenine G (Schultz Farbstofftabellen, Leipzig 1931, 7th ed., vol. 1, No. 726). The intermediate layer prevents the yellow dye from penetrating into the middle layer. The result of the processing is that a correctly colored positive three-color-picture is obtained.

Example 3.—Alternatively, the three layers used in Example 2 may be coated on a transparent support in such a manner that the blue-sensitive layer is immediately adjacent to the support; then follows the first intermediate emulsion layer sensitive to infrared, then the green-sensitive layer, follower by the intermediate layer containing exposed silver halide, and finally by the red-sensitive emulsion layer which in this case is the surface layer. The exposure is, effected through the support. The support itself contains a substance absorbing infrared light or this substance may be in a colorless or slightly colored colloid layer coated on that side of the support that is opposite to the light-sensitive emulsion layers. The object of this measure is to render the film capable of being exposed in the camera without any further precautions against the penetration of infrared light into the light-sensitive layers during exposure. When a multilayer film of this nature is employed, the sequence of dyeing is to be reversed, i. e. the three layers are all to be dyed yellow first and then the film is exposed to infrared light and again developed with the hardening developer. After the two outer layers have been decolorized, they are re-dyed magenta and finally, after decoloring the surface layer, the latter is re-dyed blue-green. The exposure to infrared light of the intermediate layer that is to be tanned is effected from the side away from the infrared-absorbing support.

If, on the contrary, it is a question of printing material, in the course of whose exposure the exclusion of infrared light presents no particular difficulty, the reversed order of the layers similar to that described in second example, has the advantage that even an opaque, e. g. paper, support may be employed. The support should be coated with a protecting varnish.

The essence of the invention is the employment in a light-sensitive material of the intermediate layers and more particularly of intermediate layers which are uniformly exposed or which may be uniformly exposed owing to their being sensitive to infrared light. Such intermediate layers are not exposed at the same time as the layers destined to record the color-selection images, but are afterwards exposed to a uniform light and developed by a tanning process to serve as a protective intermediate layer during the treatment in the baths employed to produce the colored part-images. In a somewhat similar manner the pre-exposed or fogged intermediate layers yield a protection layer when bleached with a tanning bleacher. The colored part-images may be obtained in various ways of which the example given above illustrates but one form not intended to limit the scope of the invention. In order to

mention a different coloring process the so-called colored development may be used for the illustration of which the following example, describing for the sake of simplicity a two-color-process, may be given.

Example 4.—Two differently sensitized layers are used with an infrared-sensitive intermediate layer between them. The film after having been exposed to a colored object with the exclusion of infrared light is developed with a developer of the kind which simultaneously and in situ with the silver image gives an azo-methine dye. The film is uniformly and thoroughly exposed to infrared light and developed by a tanning developer. Thereafter, the dye in the surface layer is decolorized by an acid solution and the film illuminated by white light. This renders the silver halide developable and now the film is developed by a color developer yielding a different dye. The silver and silver halide is removed by Farmer's reducer and a two-color-image is obtained in which the surface layer contains a colored positive record of one color sensation and the lower layer a differently colored negative record of a second color sensation. By printing and an analogous treatment a two-color-positive can be obtained.

What is claimed is:

1. A process of producing multicolor images from an exposed light-sensitive multilayer material having a support and at least three gelatin layers in superposition on said support, two of said layers containing latent photographic image records constituting two different part images of the multicolor image and one of said layers being an infrared-sensitive intermediate silver halide emulsion gelatin layer between said two layers, which comprises developing the latent images with a color developer which act to form the same azo-methine dye within the image-bearing layers, exposing the material to infrared light and developing the exposed silver halide with a tanning developer which acts to tan the gelatin in situ with metallic silver formed within the intermediate layer and thereafter decolorizing the dye image within the outer layer, exposing the film to white light, developing the outer layer with a color developer yielding a different color and removing the silver from said image-bearing layers and from said intermediate layer.

2. A process of producing multicolor images from an exposed light-sensitive multilayer material having a support and at least three gelatin layers coated on one side of said support, two of said layers containing developed silver image records constituting two different part images of the multicolor image, both image records being dyed the same color with a destructible dye and one of said layers being an intermediate layer between said image-bearing layer which contains an evenly distributed substance including silver, which comprises treating the material with a tanning solution which acts in conjunction with said evenly distributed silver substance to tan the intermediate layer uniformly, and thereafter treating the outer layer with a solution to completely destroy the dye therein, and forming a dye image of a different color in proportion to the photographic image record contained in said outer layer.

3. A process of producing multicolor images from an exposed light-sensitive multilayer material having a support and five gelatin layers in superposition on said support, three of said layers containing photographic image records constituting three different part images of the multicolor image, another being an intermediate gelatin layer between the two outer image-bearing layers containing uniformly exposed silver halide, and another being an intermediate layer between said image-bearing layers and the third image-bearing layer comprising infrared-sensitive silver halide, which comprises coloring all of the image-bearing layers with the same destructible dye, exposing the material with infrared light and treating the material with a tanning developer which acts to tan the gelatin in situ with the developed silver to thereby tan the last-mentioned intermediate layer uniformly, treating the two outer layers with a solution to completely destroy the dye therein, forming dye images of a different color in proportion to the photographic image records contained in said two outer layers, treating the material with a tanning bleacher, treating the outermost of said image bearing layers with a solution to completely destroy the dye therein, forming a differently colored image in proportion to the photographic image record contained in said outermost layer and removing the silver from said image bearing layers and from said intermediate layers.

4. A process of producing multicolor images from an exposed light sensitive multilayer material having a support and at least three gelatin layers coated on one side of said support, two of said layers containing developed silver image records constituting two different part images of the multicolor image and one of said layers being an intermediate layer between said two layers which contains an evenly distributed substance including silver, which comprises coloring the image portions of said image bearing layers with the same destructible dye, treating the material with a tanning solution which acts in conjunction with said evenly distributed silver substance to tan the intermediate layer uniformly, and thereafter treating the outer layer with a solution to completely destroy the dye therein, and forming a dye image of a different color in proportion to the photographic image record contained therein.

5. A process of producing multicolor images from an exposed light sensitive multilayer material having a support and at least three gelatin layers coated on one side of said support, two of said layers containing developed silver image records constituting two different part images of the multicolor image and one of said layers being an intermediate layer between said two layers which contains an evenly distributed substance including silver, which comprises coloring said two layers with the same destructible dye, treating the material with a tanning solution which acts in conjunction with said evenly distributed silver substance to tan the intermediate layer uniformly, and thereafter treating the outer layer with a solution to completely destroy the dye therein, forming a dye image of a different color in proportion to the photographic image record contained in said outer layer, the photographic image in said underlying image layer being converted to a dye image by destroying said destructible dye in proportion to said photographic image at a point in said process following the coloring of said two layers.

6. A process of producing multicolor images from an exposed light-sensitive multilayer material having a support and at least three gelatin

layers coated on one side of said support, two of said gelatin layers containing developed silver image records constituting two different part images of the multicolor image and one of said layers being an intermediate layer between said two layers which contains uniformly distributed metallic silver, said intermediate layer being colored by a dye which can be bleached in the presence of metallic silver, which comprises uniformly coloring the image-bearing layers and the intermediate layer with a dye which can be bleached in the presence of metallic silver, treating the material with a dye-destroying agent which acts to decolorize the parts where silver is present without entirely eliminating said silver, treating the material with a solution which acts to transform the remaining silver into silver salt and simultaneously to tan the gelatin where silver is present, treating the surface layer with a dye-destroying solution which acts without the intermediate of silver and thereafter treating the decolorized surface layer to convert the tanned relief to a colored image.

7. A process of producing multicolor images from an exposed light-sensitive material having a support and at least three gelatin layers coated on one side of said support, two of said gelatin layers containing developed silver image records constituting two different part images of the multicolor image and one of said layers being an intermediate layer between said two layers which contains uniformly distributed metallic silver, which comprises uniformly coloring the image-bearing layers and the intermediate layer with a dye which can be bleached in the presence of metallic silver, treating the material with a dye-destroying agent which acts to decolorize the parts where silver is present without entirely eliminating said silver, treating the material with a solution which acts to transform the remaining silver into silver salt and simultaneously to tan the gelatin where silver is present, treating the surface layer of said material with a dye-destroying solution which acts without the intermediate of silver and thereafter treating the decolorized surface layer to convert the tanned relief to a colored image.

8. A process of producing multicolor images from an exposed light-sensitive multilayer material having a support and at least three gelatin layers coated on one side of said support, two of said layers containing developed silver image records constituting two different part images of the multicolor image and one of said layers being an intermediate layer between said two layers which contains uniformly distributed metallic silver, said intermediate layer being colored by a dye which can be bleached in the presence of metallic silver, which comprises uniformly coloring the image-bearing layers and the intermediate layer with a dye which can be bleached in the presence of metallic silver, treating the material with a dye-destroying agent which acts to decolorize the parts where silver is present without entirely eliminating said silver, treating the material with a solution which acts to transform the remaining silver into silver salt and simultaneously to tan the gelatin where silver is present, fixing the film and drying, treating the surface layer with a dye-destroying solution which acts without the intermediate of silver and thereafter treating the decolorized surface layer with a water soluble dye to color the unhardened places.

9. A process of producing multicolor images from an exposed light-sensitive multilayer material having a support and at least three gelatin layers coated on one side of said support, two of said layers containing developed silver image records constituting two different part images of the multicolor image and one of said layers being an intermediate layer between said two layers which contains uniformly exposed and developed silver halide, which comprises uniformly coloring the image-bearing layers and the intermediate layer with the same dye which is capable of being destroyed with the aid of metallic silver, treating the material with a dye-destroying agent which acts to destroy the dye where silver is present without entirely eliminating said silver, thereafter treating the material with a tanning bleacher which acts to tan the gelatin in situ with metallic silver and simultaneously to convert the silver into silver salt, and thereafter treating the surface layer with a solution to completely destroy the dye therein, forming a dye image of a different color in proportion to the image record contained in said surface layer, and removing the silver salt from said image bearing layers and from said intermediate layer.

10. A process of producing multicolor images from an exposed light sensitive multilayer material having a support and at least three gelatin layers coated on one side of said support, two of said layers containing developed silver image records constituting two different part images of the multicolor image and one of said layers being an intermediate layer between said two layers which contains an evenly distributed substance including silver, which comprises coloring said two layers with the same destructible dye, treating the material with a tanning solution which acts in conjunction with said evenly distributed silver substance to tan the intermediate layer uniformly, and thereafter treating the outer layer with a solution to completely destroy the dye therein and forming a dye image of a different color in proportion to the photographic image record contained in said outer layer.

11. A process of producing multicolor images from an exposed light-sensitive multilayer material having a support and at least three gelatin layers coated on one side of said support, two of said layers containing latent silver halide image records constituting two different part images of the multicolor image and one of said layers being an infrared-sensitive intermediate silver halide emulsion gelatin layer between said two layers, which comprises developing the latent images with a color developer which acts to form the same azo-methine dye within the image-bearing layers, exposing the material to infrared light and developing the exposed silver halide with a tanning developer which acts to tan the gelatin in situ with metallic silver formed within the intermediate layer and thereafter decolorizing the dye image within the outer layer, exposing the film to white light, developing the outer layer with a color developer yielding a different color and removing the silver from said image-bearing layers and from said intermediate layer.

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