Aug. 17, 1943. G. P. GRANT, JR 2,327,304

COLOR PHOTOGRAPHY

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Fig. 1.

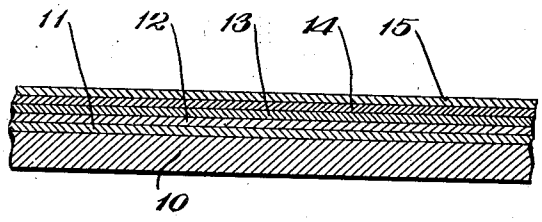
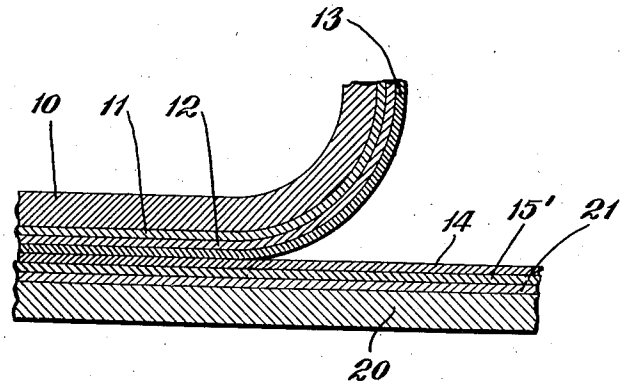


Fig. 2.



INVENTOR
GARNET PETER GRANT JR
BY
Cousins & Cousins
ATTORNEYS

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COLOR PHOTOGRAPHY

Garnet Peter Grant, Jr., Silvermine, Comm., assignor to Grant Photo Corporation, New York, N. Y.

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5 Claims. (Cl. 95—2)

This invention relates to color photography and methods of making colored prints from color separation exposures obtained either directly from exposure in a camera or from color transparencies.

The invention comprehends a sheet or base material having a special type of photosensitive surface on which separate images are projected to create the desired color separation exposures which are treated in situ to produce positive prints which may be quickly and easily transferred to a backing in order to produce the finished colored print.

In color photography three separate negatives are made, a special filter being disposed in front of each negative at the time the picture is taken so that one of the three negatives is affected by the red light rays, one by the green and the other by the blue. In order to obtain such negatives the exposed film must be developed, fixed in hyposulphite, washed and dried. One way of exposing a film is in a "one shot" color camera consisting of a lens related to a system of prisms and mirrors, so that the image is split into three parts, each having its particular color filter. The negatives so obtained are called color separation negatives and usually they are made on regular film.

There are two generally used commercial processes of making colored photographs:

The first is the so-called "chromatone" process which utilizes a photographic emulsion disposed upon a "stripping" layer in such fashion that such emulsion may be stripped from a base after having been suitably treated. This process proceeds generally by first making three color separation negatives as above outlined, then, by suitable exposure, making a print from each such negative on a special paper provided with such an emulsion. After suitably treating the emulsion to give the image developed therein a desired color, and stripping it from its base, floating it away, and finally superimposing it on a backing, other colored images are similarly created, their emulsions stripped, and superimposed in registry with the first emulsion in order to construct a complete color print.

The second color process is sometimes known as the "wash-off" process. This differs from the process above described in that a different type of paper is used to make the separate prints which are made on what is termed "relief" emulsion. This permits the gelatin to harden in the areas where the light has affected the photo sensitive material. The process is carried out by immersing the print in warm water to wash off the non-hardened gelatin, drying the remainder and forming it into a matrix from which an image may be printed in relief, applying a coloring material to the surface of the matrix and printing one color therefrom on a specially treated white paper, and then printing the other colors from similarly prepared matrices so that such colored prints are in registry with the first print. In this way the natural color print is recreated.

It will be noted that in both the above described processes separate prints are made from the color separation negatives, and such negatives are discarded and of no use in the further steps of the process.

The procedure outline, although yielding satisfactory results when properly carried out, are expensive and time-consuming. An ordinary 8" x 10" enlarged print made by either process requires two to four hours of time, a large part of which is consumed in the production and treatment of the negatives, which tends to increase the price for which the ultimate product can be sold to the consumer. Moreover, it is difficult to handle the thin emulsions and to secure an accurate registration of the separate components of the finished print.

Objects of the invention are to simplify and render less expensive and more rapid the production of color prints, to facilitate the handling of the thin photosensitive layers required thereby, to insure complete and accurate registration of the component parts of the colored print, and to provide a photosensitive sheet and a method by means of which such objects and advantages may be achieved. Other objects of the invention and the advantages thereof will more clearly appear when reference is had to the following specification and claims, when considered in the light of the accompanying drawing.

The invention consists in the construction, combination and arrangement of parts of the product and the steps of the process, as herein illustrated, described and claimed. In the accompanying drawing, forming a part hereof, are illustrated two embodiments of the invention, in which drawing similar reference characters designate corresponding parts, and in which:

Figure 1 is a greatly enlarged fragmentary section of one type of photosensitive sheet by means of which the process of the invention may be carried out; and,

Figure 2 is a similar view showing how such a sheet, after having been processed according to the invention, may be related to a backing so that a colored positive may be stripped therefrom and adhered to such backing.

Adverting now to the photosensitive sheet by means of which the process of the invention may be carried out, the same may be broadly described as comprising a base or support, a panchromatic, positive reversal emulsion and a stripping layer uniting such base with said emulsion. More particularly, the sheet may be constructed as indicated in Figure 1 and may consist of a

base 10 of paper, Celluloid or glass coated with a suitable filler 11 in order to fill in the pores and provide a smooth uniform surface. The base may be coated with or dipped into a waterproofing compound 12 such as lacquer or wax.

A stripping layer 13 comprising a substance, such as glue soluble in water or in another suitable solvent, may be provided on top of the coating 12. Under certain conditions the filler 11, the waterproof layer 12, or binding layer 14 hereinafter described may likewise serve as a stripping layer.

A binding layer 14 of a transparent material having an affinity for a gelatinous photosensitive emulsion and for the stripping layer 13, such as collodion, or gelatin admixed with a solvent such as acetone, may advantageously be applied over the coating 13, and on top of the layer 14 is disposed a single sensitized emulsion 15, of the panchromatic positive reversal type. By "positive reversal" I mean that the emulsion is such that the image as projected thereon may be developed, bleached off and washed, the remainder exposed to light and re-developed, or otherwise treated in order to change the negative to a positive. A suitable panchromatic, positive reversal emulsion may comprise a precipitate of specially sensitized silver halide particles distributed throughout a coagulated gelatinous film, applied as a smooth and uniform layer. It may be made by treating the photo sensitive chemicals in a known positive-reversal type of emulsion such as that known by and sold under the trade name "Direx" by the Positype Corporation of America, with organic compounds which render the emulsion panchromatic.

It should be understood that one or more of the above mentioned layers may be omitted or the said layers may be rearranged in various ways without departing from the invention. It is important, however, that there be present on the raw paper stock or other support 10 a smooth surface or layer to which the emulsion 15 will adhere and from which it may be stripped at the conclusion of the process. For instance, the stripping and binding layers above described may be omitted and the waterproofing layer used or arranged so that it may be used to serve the purpose thereof. A waterproof layer is of advantage in order to minimize the absorption by the support of the chemicals of the photographic emulsion and treating fluids and to reduce the likelihood of relative movement between the photographic emulsion and the support caused by expansion and contraction.

Generally described, the process of the present invention proceeds by making three color separation exposures on separate pieces of sensitized material of the nature described. The images created by exposures of the emulsion to light through the optical system of a camera, are developed, and instead of being fixed, washed and dried as in the prior art, they are reversed from negatives to positives, treated to impart a desired color thereto, and then each is pressed in face to face relationship against the surface of a previously prepared backing and adhered thereto.

The backing may be constructed as illustrated in Figure 2 and may comprise a sheet 20 having a gelatinous coating 21 on its surface, to which the first colored positive, indicated at 15^1, adheres. The colored positive having been adhered to the backing, the base or support 10 is stripped therefrom.

The other positives, toned with suitable colors, are then applied in registry with the first and their bases or supports 10 successively stripped off until all three of the colored positives are applied to the backing.

A feature of the invention is that negative films are each created on their original bases or supports, reversed, toned and otherwise treated in situ upon such support, and only after they have been completed in the form of separate colored positives and properly registered on a backing are they stripped from their supports. This obviates the difficulty of handling the thin emulsion films constituting the prints, except as they are secured to and upon their supports 10, and insures their complete and accurate registry.

Another feature of the invention is that it is not necessary to fix, wash and dry the negative, as in the ordinary color processes, nor is it necessary to make a separate exposure through the negative onto special strippable paper or otherwise, in order to obtain separate positive images.

Coming now to a more detailed description of the process, I may proceed as follows:

1. I first make three color separation exposures by exposing three panchromatic, positive reversal sheets such as are shown in Figure 1, to focused images from a suitable lens system. This may be accomplished in a "one shot" camera by placing a color filter in front of each photosensitive sheet; for instance, I may use a green filter in front of one sheet in order to filter out red and blue light, a blue filter in front of another to filter out the yellow and red light, and a red filter in front of the third to filter out the blue-green light.

2. After each sheet is so exposed the impressed image is developed by a suitable developer and rinsed. This removes the salts from the areas where the light has effected a chemical change in the emulsion, and produces a negative.

3. The sheet is immersed in a bleaching solution such as potassium dichromate or permanganate, and sulphuric acid in order to remove the developed image of the negative.

4. It is again immersed in a clearing solution such as sodium sulphite or bisulphite to remove the yellow residue left by the bleaching.

5. The negative is then "flashed;" that is, it is exposed to a white light in order to activate the areas which were originally unaffected by the light image.

6. The "flashed" photosensitive layer is then redeveloped; that is, the areas affected by the flash are developed and rinsed. At this point the reversal is complete and the sheets carry positives instead of negatives. They have black and white positive images, each representing the densities of one of the three basic colors, red, yellow and blue.

7. Each positive is "toned;" that is, a color is imparted according to the nature of the particular image, whether it received the red, yellow or blue rays. One way of toning is as follows:

(*a*) Immersing in a bleaching solution such as potassium ferrocyanide and hyposulphite, in order to convert the metallic silver to silver ferrocyanide.

(*b*) Immersing each positive into a special solution in order to replace the silver in the silver ferrocyanide with some metal which produces a salt of the desired color, either red, yellow or blue. Thus each positive is colored with one of the basic colors.

8. A backing paper 20 (see Figure 2), is soaked

in water to soften the gelatinous coating 21 thereon and the first of the colored positives is brought in face to face relationship with the backing 20 and adhered thereto.

9. If one or more of the intermediate layers 11, 12, 13 or 14 have not been sufficiently softened or loosened by the preceding treatments, the assembly may be immersed in a solution called a "stripping" solution, which is a solvent for any one of such layers or coatings.

10. The backing 10 plus such adhering coatings as have not been dissolved or softened, are stripped from the paper 20, as indicated in Figure 2. In this figure stripping layer 13 is shown intact for facility of illustration, but in practice this layer is at least partially dissolved in the stripping solution. The second color positive is registered with the first, dipped, if necessary, in the stripping solution and stripped off as indicated. The result is two color films on the backing 20.

11. The third colored positive is similarly registered and stripped so that the final result is three of the colored films in registered relationship on the backing 20. This produces the finished colored print in which the original colors are re-created.

The original sheet 10 has been retained throughout the process and not discarded until after the top photosensitive film has changed into a colored positive and been properly registered on backing 20, and adhered thereto. No negatives have been discarded and no separate positives have been required inasmuch as the original negatives have been reversed into positives. The entire process may be carried out with a minimum expenditure of time and materials.

It is pointed out that although it is advantageous to retain the emulsion in association with the base or support 10 up to the time the emulsion is adhered to the backing, it is not necessary to do this. The emulsion may be stripped from its support at any predetermined point in the process, with proportionate benefits as to ease in handling. In the event the emulsion is stripped from its support prior to its registration upon and adhesion to the backing, the same is preferably floated away from the support after stripping. A transparent strengthening film of collodion, which may comprise the binding layer 14, may be provided adjacent the emulsion in order to facilitate this operation.

One way of toning the positive by converting the silver particles constituting the image in the emulsion into a colored salt, is as follows:

For obtaining a red image of the positive, the following solutions are prepared:

Solution A:

Nickel nitrate	grams	5
Potassium citrate	do	15
Water	c. c.	100

Solution B:

Potassium ferricyanide	grams	2

Solution C:

Saturated solution of dimethyl-glyoxime in methyl (wood) alcohol	c. c.	5
0.4% sodium hydroxide	c. c.	5
Water	c. c.	500
Concentrated ammonia	drops	5 to 6

Solutions A and B are freshly mixed, combined and then acidified with a few drops of dilute nitric acid, and the sheet or print is immersed therein until bleached. It is then washed and placed in Solution C for several minutes, whereupon it is removed and washed.

For obtaining a blue tone a solution comprising the following is prepared and the redeveloped print immersed therein:

Ferric ammonia citrate	grams	2
Potassium ferricyanide	do	2
Tartaric acid	do	7
Water	c. c.	500

Since this toner gives considerable intensification of the image, the print should be under printed but fully developed.

For yellow the following solutions may be prepared:

Solution A:

Acetic acid (glacial)	c. c.	5
Lead nitrate	grams	3
Potassium ferricyanide	do	2
Water	c. c.	200

Solution B:

Potassium dichromate	gram	1
Water	c. c.	200

The print is bleached in solution A, washed and then placed in Solution B for several minutes. Strong ammonia water is added drop by drop until the color changes from orange to light yellow.

It should be noted that it is not necessary to "fix" the print since the toning procedure affects all parts of the image produced by the flashing and redeveloping operations. The reversal has already eliminated the parts that the plain hyposulphite solution comprising the ordinary fixing bath is intended to remove.

Another way in which the positive image may be colored or toned is as follows:

After the sheet is flashed it is immersed in a special redeveloping solution comprising, for blue, 10 parts of Solution A, made up of:

Solution A:

Sodium sulphite	grams	18
Sodium carbonate	do	40
Potassium bromide	do	1
2 amino-5 diethylamino toluene monohydrochloride	do	1
Water to make	liter	1

and one part of a 1% solution of 2,4-dichloro-1-naphthol in ethyl alcohol.

For yellow the special redeveloper may consist of 10 parts of the above described Solution A, and 1 part of a 1% solution of acetoacet-2,5-dichloroanilide in ethyl alcohol.

For red, 10 parts of Solution A may be used with 1 part of a 1% solution of p-nitrophenylacetonitrile in ethyl alcohol.

In each of the three foregoing treatments the redeveloper changes the silver halide to metallic silver and permits the oxidation product to combine or couple with the organic coupling compound of the added solution to produce an insoluble dyestuff which is deposited in the emulsion adjacent the silver image, the latter being removable if desired by bleaching it out in a solution known as "Farmer's reducer," which does not affect the dye images.

Still another way in which the positives produced by the practice of the present invention may be reversed and toned, is by direct chemical action, as by immersing the sheet, after the clearing operation of hereinbefore numbered 4, in suitable polysulphides in order to convert the

silver halide of the positive to salts of the desired color.

It is to be understood that the specific constructions, operations and compositions above described are illustrative merely and do not limit the invention. Such changes and modifications as are apparent to those skilled and in the art may be made without departing from the invention as herein shown, described and claimed.

Having thus fully described the invention, what is claimed as new and desired to be secured by Letters Patent is:

1. The process of making colored prints comprising forming a plurality of color separation exposures on a panchromatic, positive reversal strippable emulsion secured to a support, developing said exposures and converting them into positives, coloring said positives, adhering one of said positives to a backing, stripping the support therefrom, and thereafter adhering another positive to the first in registered relationship therewith and stripping its support therefrom.

2. The process of making colored photographic prints comprising forming a plurality of color separation exposures on a panchromatic, positive reversal emulsion secured to a support, developing said exposures, reversing the same and therby forming positives, coloring said positives, adhering one of said positives to a backing, stripping the support therefrom, adhering another positive to said backing in super imposed and registered relationship with the first and then stripping its support therefrom.

3. The process of making colored photographic prints comprising forming a plurality of color separation exposures on a panchromatic, positive reversal emulsion secured to a support, developing said exposures, reversing the same and thereby forming positives, coloring said positives, adhering one of said positives to a backing, stripping the support therefrom, adhering another positive to said backing in superimposed relationship with the first, stripping its support therefrom, adhering a third positive to said backing in superimposed and registered relationship with the first two positives and then stripping its support therefrom.

4. The steps in the process of making colored photographic prints which steps comprise supporting a panchromatic, positive reversal emulsion on a sheet, disposing separate sheets in a camera, separately activating the emulsion on each sheet with the light rays comprising one of the primary colors, and thereby forming three color separation exposures, developing and reversing each exposure and thereby forming positives, coloring each positive and then transferring the same in superimposed relationship to a backing, retaining the emulsion on the first mentioned sheet until the transfer to the backing is completed.

5. The steps in the process of making colored photographic prints which steps comprise supporting a panchromatic, positive reversal emulsion on a sheet, disposing separate sheets in a camera, separately activating the emulsion on each sheet with the light rays comprising one of the primary colors, and thereby forming three color separation exposures, developing and reversing each exposure and thereby forming positives, coloring each positive, adhering one colored positive to a backing and stripping said sheet from such positive and thereafter registering and adhering a second positive in superimposed relationship to the first and stripping the supporting sheet therefrom.

GARNET PETER GRANT, JR.