March 19, 1946. L. S. TRIMBLE 2,396,726

PROCESS FOR PRODUCING COLOR PRINTS AND PRODUCTS

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Fig. 1

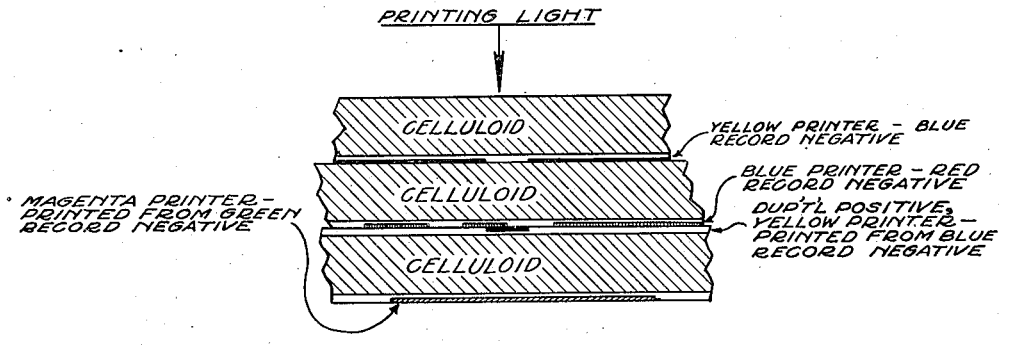
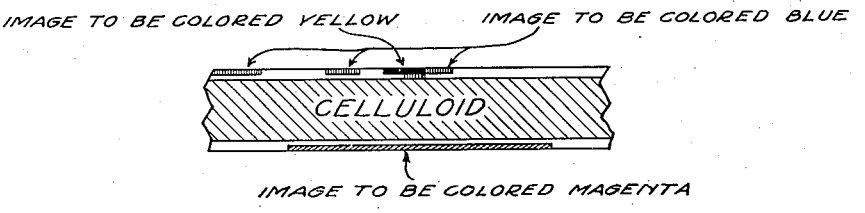


Fig. 2



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PROCESS FOR PRODUCING COLOR PRINTS AND PRODUCTS

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7 Claims. (Cl. 95—2)

My invention relates in general to the art of color photography with particular reference to new and novel methods for producing combinations of photographic images and separately coloring them to produce color positive films suitable for use in motion pictures. While the process of my invention is applicable to both still and motion picture photography, it finds its widest range of application in the latter branch of the art, and consequently I will confine my description of a preferred form of my invention to its adaptation in motion picture transparencies, it being understood that whenever the term "film" is used, it is meant to include all types of film, photographic plates, and paper for all branches of photography.

In producing colored motion pictures by subtractive methods, one of two types of film is generally used; first a film which comprises a base with a layer of emulsion upon each side thereof, or second, a film comprising a base with a layer of emulsion upon only one side thereof, which said layer may have the same sensitivity throughout or may have a varying or stratified sensitivity, depending upon the use to which it is to be put. In producing positive prints in color, by the use of film having an emulsion layer on one side only, it is usual to have the emulsion sensitized substantially uniformly throughout, one photographic color value image being produced in the upper or outer stratum of the emulsion layer by printing from a negative to the face of the emulsion, and a second photographic image of another color value is printed or produced in the lower or inner stratum by printing through the base from another color value negative. If the process is a two color process, this constitutes the entire printing step, however, if a three color process is being followed various methods may be employed for producing three images in the emulsion layer. Imbibition is a common procedure whereby a relief image previously saturated with dye is placed in contact with the positive film which receives the dye in proportion to the matrix image density for a given contact time and temperature. Several methods have been utilized that render a printed and developed image transparent so that a third image may be printed through this first image. If a double emulsion film, the so-called duplitized positive, is being used two images may be produced on one side of the base and a third image on the opposite side.

Various color processes have been promulgated which utilize two images in separate strata of a single emulsion and color the images substantially complementary colors. I have found, however, that it is very difficult to control the treatment of two images in separate strata of the same emulsion layer so as to produce separate colored images which are satisfactory, since in the usual known processes of this type, the step or steps which are used in coloring the outer image usually affect the inner image to its detriment, or yield an outer image which is subsequently modified or otherwise damaged by the treatment prescribed for the inner image.

An object of my invention is to provide a process of color photography whereby a satisfactory combination of two images in a single emulsion layer may be utilized in combination with a third image.

Another object of my invention is to provide a process whereby the production of two images in the same strata, as well as their subsequent conversion to substantially complementary colors, is accomplished in the case of either image as though the other image was not present.

Another object of my invention is to provide a process in which an image may be printed in an emulsion through an image already present in said emulsion without substantially altering its form and as though said first printed image had not been present.

Another object of my invention is to provide a process of treating a silver image chemically whereby said silver image is rendered unaffected by a subsequent treating solution normally capable of reacting with said silver image.

In a preferred form of my invention, I produce two images, a yellow color value image and a magenta color value image in the outer strata on each side of a double coated or duplitized film by simultaneously printing the two images in register from suitable color separation negatives. These images are developed in the usual manner so that they both comprise free silver. After sufficient wash to remove all traces of the developing solution the images are chemically sealed in such a manner that a suitably proportioned blue tone capable of converting a silver image into a blue color value image of Prussian blue will have no effect upon the above images. This is accomplished by treating the above silver images with a solution comprising a bichromate of an alkali metal, and an alkali bromide or chloride. The essential action depends upon the presence of the negative ions. Any soluble salt of a chromate or bichromate may be used as well as any soluble salt of a bromide or chloride. Iodide produces the desired effect as well but converts the silver halide to silver iodide which is not very responsive

to subsequent exposure and development. The pH of the solution must be adjusted such that the silver image will not be bleached to a silver halide; the exact value will depend upon the temperature, immersion time, and gelatine hardness. In general any pH value above 3.5 is satisfactory. The exact nature of such sealing action is not known. It may be that of gelatine hardening by virtue of chromium oxide formation, or it may be an actual silver grain coating of chromium oxides or hydroxides. The chemical concentration of the two constituents may be varied considerably depending upon the immersion time, solution temperature, and film agitation. I have found the best results using a range of 2 to 3 per cent of potassium dichromate and 1 to 2 per cent of potassium bromide coupled with an immersion time of about nine minutes. This treatment is followed by a suitable wash to remove the above solution after which the film is dried. Inasmuch as there has been no fixing step and the film is still light sensitive, all work must be conducted under suitable safe lights.

The blue color value image is printed onto the film in the following manner. First the sound track is printed utilizing an ultra violet filter in the sound printer. This is customary in black and white work; it has the effect of restricting the image to the surface of the stock, hence by virtue of restricted dispersion, the image is quite sharp. This track and the blue color value image may be printed on either side of the positive stock, in the preferred form it is printed on the side carrying the yellow color value image. This blue color value image is now printed from a suitable color separation negative, through the yellow negative, or a duplicate thereof, having an equal gamma or contrast as the positive yellow image. See Figure 1. The formerly printed and treated yellow positive 1, and the yellow printer 2 which is the blue record negative when combined with the above conditions results in a perfect neutral density throughout the picture area; that is, a mask such that the yellow positive image is rendered entirely ineffective. It is then only necessary to increase the printing light intensity sufficiently to penetrate through this neutral density and print the blue color value image. The silver images representing the yellow positive and the yellow negative should be of equal gamma or contrast. The actual grain condition of the treated silver image as well as the exact position of the images on the curves representing the sensitometric characteristics of the negative and positive stocks combine to make a slight deviation from the above condition allowable. It will be understood, however, that a uniform density field is required, and not merely a combination of negative and positive as is often utilized to give a color corrected image. Printing through the combined negative and positive for color correction purposes results in an image, whereas a print made through the correct combination discussed above will produce a uniform field of exposure just as though the two films had been replaced by a neutral density filter. The preferred form of printing is shown in Figure 1. This results in a very sharp image. If the yellow printer and the positive emulsion were adjacent, the blue image printed through this combination would suffer in sharpness by virtue of the light dispersion through the negative base and emulsion. A grey base or anti-halation negative, of course, helps this situation, but I have found the sharpest image is obtained under the conditions of Figure 1 and that the blue color value image is produced as though the yellow color value image had not been present. This blue color value image and sound track are developed to suitable contrasts and the film well washed. The result is shown in Figure 2.

The next step in my process is to convert this last developed blue color value image to Prussian blue in a blue toning solution capable of producing complete image conversion without affecting the two images sealed by the above mentioned method. A typical formula which completes the image conversion in approximately four minutes is

Ferric ammonium oxalate	grams	6
Potassium ferricyanide	do	6
Sulfuric acid	ml	1
Water to make	liter	1

This is followed by a wash of about four minutes, then by complete fixation of all silver salts present by a suitable bath of sodium thiosulfate using a small amount of sodium sulfite or bisulfite as is customary in a non hardening hyposulfite. This step requires about five minutes and results in a clear film bearing two silver images representing the yellow and magenta color aspects and a Prussian blue image representing the blue color value aspect. The remaining steps involve converting the magenta and yellow color value images to their respective colors. Several methods are available. The silver images may be converted to toned images such as nickel dimethyl glyoxime and cadmium sulfide, or they may be converted to suitable mordants for basic dyes, such as vanadium ferrocyanide, copper ferrocyanide, or silver iodide, or one may be dyed and the other toned. By floating each side of the film on the respective basic dye solutions the proper colors are adsorbed upon the mordants. My preferred form involves basic dye mordanting because of the wide range of colors available. The silver images are converted to silver iodide in a bleach of the following composition:

Iodine	grams	2
Potassium iodide	do	50
Sodium acetate	do	5
Acetic acid	ml	5
Water to make	liter	1

In the claims I use the term "certain treating solutions" to include the use of either a single certain treating solution or a plurality of certain treating solutions.

This is followed by a clearer of 5% of sodium bisulfite and a short wash. Standard dyes such as Rhodamine and Auromine are suitable for adsorption upon the silver iodide mordant. The film is well washed to remove excess dye from the gelatine and dried. The result is a three color positive capable, upon projection, of reproducing the original subject in accurate color rendition.

While I have described one preferred form of my invention, the principle of printing an image in the described manner has many other useful applications. Furthermore, two images may be printed in such a manner on a single emulsion film, with subsequent coloring of these two and the production of a third image by imbibition. This of course is applicable to duplitized film where the imbibed image is placed on the non image bearing emulsion. In another modification two images may be printed, developed, one side of the film floated on a solution whereby the image on that side is rendered unaffected by a

subsequent treating solution, the film washed and dried, a third image printed in the manner described hereinabove, said image developed, and the three images separately toned. The difference is that in this case only one image is treated to render it impervious to a subsequent treating solution so that by suitably composing toning solutions having differing oxidation potentials, a modified sequence of coloring is available.

From the foregoing description the uses, advantages, and operation of my invention will be readily understood by those skilled in the art to which the invention appertains. While I have described certain forms of my invention which I now consider to be the best embodiments thereof, I desire to have it understood that the forms shown are merely illustrative and that the invention is not to be limited to the details disclosed herein, but is to be accorded the full scope of the appended claims.

I claim:

1. A process of producing three color positive prints which comprises printing in register from suitable color separation negatives two color value images on a transparent support carrying a silver halide emulsion layer on each side, said images being printed on the outer surfaces of said emulsion layers, developing said images, treating said images with a solution comprising a bichromate of an alkali metal and a chemical selected from the group consisting of alkali chlorides and alkali bromides, the ingredients being in such concentration and the pH value being so adjusted that said images are not substantially altered from metallic silver but said images are rendered unaffected by certain treating solutions normally capable of reacting with said images, printing one other color value image on said transparent support already carrying two silver images through and in register with one of said first mentioned images and the negative from which said one image was printed in such a manner that said other color value image is produced in back of and interpenetrating with said one image but substantially as if no other image had been present, developing said last mentioned image and converting said last mentioned image to a suitable color by means of said certain treating solutions, and then converting said first mentioned images to suitable colors.

2. A process of producing three color positive prints which comprises printing in register from suitable color separation negatives two color value images on a transparent support carrying a silver halide emulsion layer on each side, said images being printed on the outer surfaces of said emulsion layers, developing said images, treating said images with a solution comprising a bichromate of an alkali metal and a chemical selected from the group consisting of alkali chlorides and alkali bromides, the ingredients being in such concentration and the pH value being so adjusted that said images are not substantially altered from metallic silver, but said images are rendered unaffected by certain treating solutions normally capable of reacting with said images, printing one other color value image on said transparent support already carrying two silver images through and in register with one of said first mentioned images and the negative from which said one image was printed in such manner that the negative to be printed is in between the positive and the negative from which said one image was printed and which negative to be printed has its emulsion adjacent to the emulsion of the positive, developing said last printed image and converting said last printed image to a suitable color by means of said certain treating solutions, and then converting said first mentioned images to suitable colors.

3. A process of producing three color positive prints which comprises printing in register from suitable color separation negatives two color value images on a transparent support carrying a silver halide emulsion layer on each side, said images being printed on the outer surfaces of said emulsion layers, developing said images, treating said images with a solution comprising a bichromate of an alkali metal and a chemical selected from the group consisting of alkali chlorides and alkali bromides, the ingredients being in such concentration and the pH value being so adjusted that said images are not substantially altered from metallic silver, but said images are rendered unaffected by certain treating solutions normally capable of reacting with said images, printing one other color value image on said transparent support already carrying two silver images through and in register with one of said first mentioned images and the negative from which said one image was printed, developing said last printed image and converting said last printed image to a suitable color by means of said certain treating solutions, and the converting said first mentioned images to suitable colors.

4. A process of producing color positive prints which comprises printing at least one color value image from a suitable color separation negative on a silver halide emulsion layer on a transparent support, said image being printed on the outer surface of said emulsion layer, developing said image, chemically treating said image in such a manner that said image is not substantially altered from metallic silver, but is rendered unaffected by certain treating solutions normally capable of reacting with said silver image, printing one other color value image on said emulsion layer already carrying at least one silver image through said first mentioned image and the negative from which said first mentioned image was printed in such a manner that the negative to be printed is in between the positive and the negative from which said one image was printed, developing and converting said last mentioned image to a suitable color by means of said certain treating solutions and converting said first mentioned image to a suitable color.

5. A process of producing color positive prints which comprises printing from suitable color separation negatives two color value images on a transparent support carrying a silver halide emulsion layer on each side, said images being printed on the outer surfaces of said emulsion layers, developing said images, chemically treating said images in such manner that said images are not substantially altered from metallic silver but are rendered unaffected by certain treating solutions normally capable of reacting with said silver images, printing one other color value image on said transparent support already carrying two silver images through and in register with one of said first mentioned images and the negative from which said one image was printed in such a manner that said negative to be printed is in between the positive and the negative from which said one image was printed and which negative to be printed has its emulsion adjacent to the emulsion of the positive, developing said last mentioned image, converting said last mentioned image by means of said certain treating solutions to a Prussian blue

image and converting said first mentioned images to dye mordanted images.

6. The method of printing a positive image from a suitable color separation negative on a silver halide light sensitive layer already carrying at least one silver positive image, one of said images being on the outer surface of the layer with unexposed silver halide below and interpenetrating it, which comprises printing one color value image through and in register with said one of said first mentioned images and the negative from which said one image was printed in such a manner that the negative to be printed is in between the positive and the negative from which said one image was printed and which negative to be printed has its emulsion adjacent to the emulsion of the positive.

7. In a process of producing color positive prints, the step of treating at least one color value silver image with a non-bleaching solution comprising from approximately two to approximately three percent of a bichromate of an alkali metal and from approximately one to approximately two percent of a chemical selected from the group consisting of alkali bromides and alkali chlorides, the pH value of said solution being above 3.5 and the time of treatment being of the order of nine minutes so that said image is not substantially altered from metallic silver but said image is rendered unaffected by certain treating solutions normally capable of reacting with said image.

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