March 5, 1968 L. J. NICASTRO 3,372,028

COLOR PROCESS UTILIZING A SINGLE LAYER SILVER HALIDE EMULSION

Original Filed Jan. 10, 1963 2 Sheets-Sheet 1

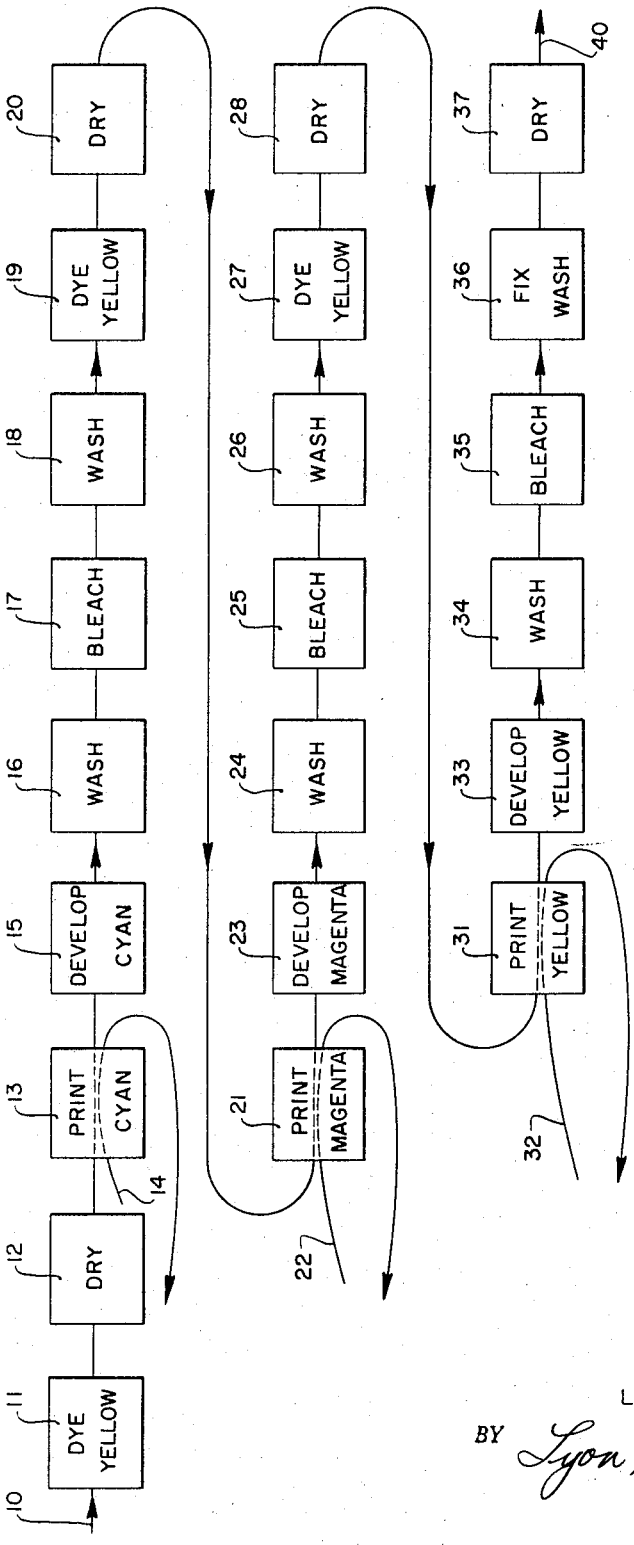

FIG. 1

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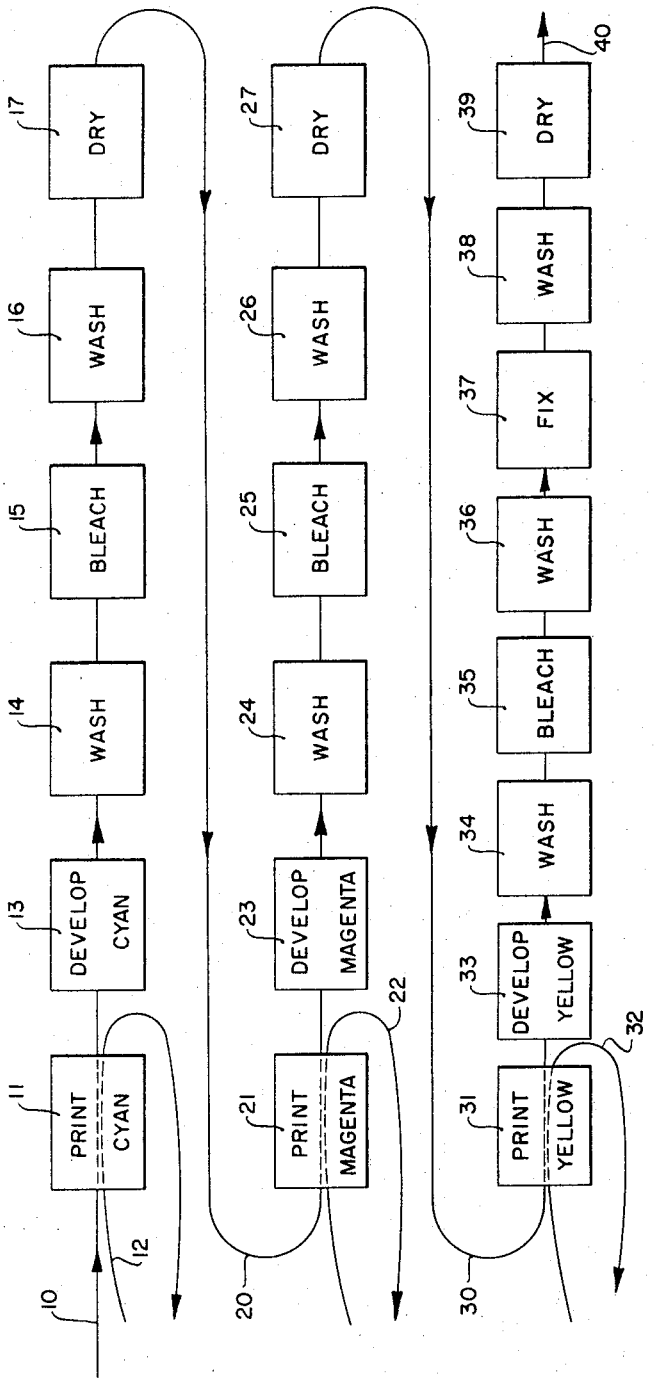

FIG. 2

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United States Patent Office

3,372,028

Patented Mar. 5, 1968

3,372,028

COLOR PROCESS UTILIZING A SINGLE LAYER SILVER HALIDE EMULSION

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Continuation of application Ser. No. 250,990, Jan. 10, 1963, which is a continuation-in-part of applications Ser. No. 81,751 and Ser. No. 81,752, Jan. 10, 1961. This application Sept. 14, 1967, Ser. No. 667,810

7 Claims. (Cl. 96—4)

ABSTRACT OF THE DISCLOSURE

This invention relates to an improved process for making photographic prints in natural color, and it is particularly directed to a process in which positive film stock having a single layer silver halide emulsion is exposed through one of three color separation negatives. There are no color couplers present in this single layer. These color separation negatives are extracted by conventional means and are black and white in form. The exposed film strip is then color developed to produce the first color which may comprise cyan, and is then chemically treated with a bleach to eliminate any latent image remaining after the first exposure and development steps. The film strip is then re-exposed through a second color separation negative, color developed and processed in a similar manner, this time producing the color magenta. The film strip is exposed for the third time using the third color separation negative, and is then color developed and processed as before to produce the yellow color. The printing apparatus in which the exposures are made is designed to maintain accurate registration. If desired, the film strip may be exposed prior to the last color development step to produce one or more sound tracks. After washing, fixing and drying, the film strip then comprises a full color print.

This application is a continuation of Ser. No. 250,990, filed Jan. 10, 1963, now abandoned, which in turn was a continuation-in-part of my copending applications Ser. Nos. 81,751 and 81,752, filed Jan. 10, 1961 both now abandoned.

Summary of invention

In accordance with the present invention, the raw film stock is also preferably treated with dye prior to the first printing step and the film strip is treated with the same dye prior to each of the second and third printing steps. The presence of this dye has been found to be important for minimizing objectionable "scatter." In another aspect, this invention contemplates that the third exposure through the third color-separation negative may be accomplished through the rear side (the carrier side) of the film strip, in order to avoid the possible masking effect of the cyan and magenta colors already present, and the benefits of the dye are useful in this operation. However, this third exposure may also be accomplished through the front of the film strip.

Other objects and advantages will appear hereinafter.

In the drawings:

FIGURE 1 is a flow sheet illustrating dye treatment.

FIGURE 2 comprises a flow sheet showing the process steps in diagrammatic form of the embodiment of the present invention wherein dye treatment is not employed.

Description of preferred embodiments

Referring to FIGURE 2, the film stock **10** which contains only a simple black-and-white, silver halide emulsion is exposed in the printer **11** through a color-separation negative **12** for the color cyan. The exposed stock then passes to the color developer station **13** where the color is developed in the conventional manner by a solution comprising diethylparaphenylenediaminehydrochloride and 2,4-dichloro-naphthol, the latter material functioning as a dye coupler. The color-developed film strip then passes through the wash station **14**. The color developing operation is allowed to proceed to a desired extent, and the operation is then interrupted by the wash bath. The film strip is then treated with a bleaching agent to insure that the latent image remaining after exposure is completely destroyed before subsequent exposure and development of another color.

It is important to remove all traces of any latent image which may remain in the silver halide emulsion following color development for cyan. This is necessary, not only to destroy the latent image but to avoid undesirable effects upon subsequent exposure for the other colors. I have found that the latent image may be entirely removed by means of a bleach solution containing potassium ferricyanide and potassium bromide in the following concentration:

	Grams
Potassium ferricyanide	100
Potassium bromide	100

Water to make one litre.

It is preferred that the bleaching operation be carried out at a temperature between 80° and 120° F., although higher temperatures may be used. It is, of course, well known that photographic emulsions generally will not withstand high temperatures without reticulation or secondary reactions taking place which are harmful. However, emulsions are now commercially available which are prehardened in the course of manufacture and for this reason will withstand temperatures of 120° F. and higher without objectionable side reactions. In general, the bleaching operation should be carried out at a temperature of at least 80° F.

The particular temperature to be used within the range of 80° F. to 120° F. depends upon several considerations. One of these is the concentration of the bleaching material. Another is the potency or activity of the developer that is subsequently to be used. For example, a magenta developer which is unusually active in developing a magenta image will produce remnants of the cyan image unless all evidence of this latent cyan image is completely destroyed. Another factor to be considered is the age of the film stock. It has been determined that the latent image may more readily be destroyed in fresh film stock than in stock which is several months old. The important factor, however, in the elimination of the unwanted latent image is the temperature at which the bleaching operation is carried out. When the temperature of the bleach solution through which the color-developed film strip passes is maintained between 80° F. and 120° F., the unwanted latent image is entirely destroyed.

Although the present invention may be practiced by using a liquid bleach bath in a conventional tank, I prefer to coat the film strip with a thixotropic gel solution in accordance with the teachings of the copending application of Harlan Baumbach filed Jan. 10, 1961, Ser. No. 81,854 entitled, Method of Using Gel Coatings for Chemical Processing of Photographic Film Strips. In such case the coating of the thixotropic bleach material

onto the film strip may be accomplished at room temperature, if desired, and the coated film strip then maintained in an otherwise empty heated tank at the desired temperature for the necessary time interval, usually about one minute. The color developed and bleached film strip then passes through the wash station 16 and then into a conventional dry box 17.

The film strip 20 emerging from the dry box 17 is then passed through the printer 21 and exposed through the color-separation negative 22 for magenta. The exposed film strip 20 then passes through the developing station 23, wash 24, bleach station 25, wash 26 and drybox 27 in the same manner as described above. The bleach material, the concentration, the temperature range and the preferred method of application are the same as set forth above. If the film strip is to be provided with a photographic sound track, this sound track may be exposed at this time, before or after printing for the yellow picture, or at any stage of operation which is convenient. The film strip 30 is exposed in printer 31 through color separation negative 32. Both sound track and yellow picture may be exposed at the same time if the negative information for picture and sound is arranged in a suitable manner.

The film strip now contains two colors (cyan and magenta) and the latent image for the yellow picture and the sound track. The film strip is passed through the developer station 33, the wash 34, and the bleach 35. If the sound track has been exposed and developed, the bleach material is applied to the picture area only. After wash 36, the film is then fixed at 37, washed at 38 and dried at 39. The full color print 40 emerges from the dry box 39. The composition of the bleach material, the concentration thereof and the temperature of the bleach operation, as well as the method of application may be the same as that previously described, but may also be of different concentration and temperature since all the bleach is to accomplish at this point is to convert the metallic silver to a compound which will be capable of being removed by the fix step 37.

Referring now to FIGURE 1, the film stock 10 contains only a single layer black and white silver halide emulsion. The stock is first treated with a suitable dye at the dye station 11. I prefer to use a yellow dye which will wash out easily, for example, tartrazene, with a concentration of 4 to 5 grams per litre. The chief consideration is that the dye must absorb light in the spectral region to which the film is sensitive. A dye such as aesculine would be suitable to absorb ultra-violet light. A grey dye could be used.

After the dye operation, the film strip is then dried in the dry box station 12. The dyed film stock is then exposed in the printer 13 through a color-separation negative 14, for the color cyan. The exposure is made through the front or emulsion side of the film strip. The exposed film strip then passes through the color developer station 15 where the color is developed as described with reference to FIGURE 2. The color developed film strip then passes through the wash station 16 and into the bleach station 17, where it is treated with a bleaching agent to insure that the latent image remaining after exposure in the printer 13 is completely destroyed before subsequent exposure and development of another color. After washing at station 18, the film strip is again treated with the same yellow dye at the dye station 19 and is dried in the dry box 20.

The film strip emerging from the dry box 20 is then passed through the printer 21 and exposed through the front side through the color-separation negative 22 for the color magenta. The film strip then passes through the developing station 23, wash 24, bleach station 25 and wash 26. The film strip is then treated with the same yellow dye solution at the dye station 27 and then enters the dry box 28.

The film strip now emerging from the dry box 28 is passed through the printer 31 and exposed through the front or rear (carrier) side through the third color separation negative 32 for the color yellow. If a photographic sound track is to be employed, it is printed onto the film strip at any suitable stage of operation. The exposure for the sound track is preferably accomplished through the front side of the film strip. The film strip then passes through the developer station 33, the wash, 34, the bleach station 35, the fix and wash 36 and the dry box 37. The film strip emerging from the dry box 37 constitutes full color print. If the photographic sound track is employed on the film strip, the bleach material at the station 35 is preferably applied to less than the full width of the film strip, leaving the sound track untreated. However, the sound track may also be bleached and redeveloped.

The yellow dye may be applied in a conventional manner by passing the film strip through a dye solution, or the yellow dye may be applied as a thin coating to the film by means of apparatus such as that shown in the copending applications of Harlan Baumbach, Ser. No. 81,893, filed Jan. 10, 1961, entitled Gel Applicator Device for Chemical Processing of Photographic Film Strips, and Ser. No. 81,894, filed Jan. 10, 1961, entitled Method of Using Gel Coatings for Chemical Processing of Photographic Film Strips. The dye need not be thickened and does not form a thixotropic gel. The coating need only be about 0.002 inch thick. Five or ten seconds of time in contact with the film strip is sufficient before blowing off the excess with a high pressure air squeegee. The film strip is then dried.

The yellow dye image does no harm to the sound track and indeed aids the quality because the scatter light which causes noise is reduced by the low penetration of the sound track exposure.

The specific color developing procedure used does not comprise a part of the present invention and any suitable procedure is permissible. For example, the developing procedure described in U.S. Patent No. 2,443,909, may be used. However, as previously noted, the photosensitive emulsion used in the practice of the present invention does not contain a dye coupler. The dye coupler is contained in the color developing material. Thus, dye couplers such as nitrophenylacetonitrile, those disclosed in Patent 2,443,-909, and others may be used.

It is also to be understood that the present invention does not involve a resensitization of previously exposed silver halide. Rather, the present invention involves the elimination of latent image remaining after exposure by a bleaching step before subsequent exposure and development. It is to be emphasized that this is an important departure from the prior art which has heretofore employed treatments which merely resensitize exposed silver halide. It is unknown to the prior art to resensitize such exposed silver halide in such a manner that all portions thereof have a uniform sensitivity. Therefore, all resensitization processes are subject to the deficiency that the product thereof is incapable of producing uniform results when the resensitized product is exposed and developed. The product of the present invention is not subject to such a deficiency.

It will be apparent to those skilled in the art that the amount and concentration of the bleach used in the practice of the present invention may be varied depending upon the characteristics of the photographic film which is used, as well as the time and temperature and other significant process conditions employed in the bleaching procedure. In general, it has been found that a concentration as low as 3.5% bleach will give satisfactory results. However, it is to be understood that the amount of bleach which is necessary for the practice of the present invention is that which is sufficient to eliminate the latent image remaining after exposure. This amount of bleach may, of course, be determined by routine experimentation.

Furthermore, the process of the present invention may be practiced as a continuous process or in separate operations, e.g., developing and printing at different times.

With respect to the dye treatment described in connection with FIGURE 1, it is to be emphasized that this dye treatment should be performed before each exposure step in order to obtain optimum results. It is believed that the importance of thisp rocedure has not previously been known to those skilled in the art and that this procedure is a significant step forward in processing photographic film.

An additional advantage of the present invention is that it permits increased process speeds. For example, exposure and other process steps may be performed at 200 ft. per minute when the bleaching material described herein is used. Other bleaches may be used and, in general, they will require the use of less rapid processing speeds.

Having fully described my invention, it is to be understood that I am not to be limited to the details herein set forth, but that my invention is of the full scope of the appended claims.

It is claimed:

1. The process of making a full color photographic print from three color-separation negatives, comprising the steps of: utilizing a film strip comprising a carrier and a single layer black-and-white sliver halide emulsion, exposing said film strip through one of said color-separation negatives to form an image, color-developing said exposed film strip for one color using a dye coupler, treating said color developed film strip with a bleach solution consisting essentially of a bromide salt and a ferricyanide salt at a temperature of at least 80° F., the concentration of said salts in the solution and the temperature of the solution being effective to entirely remove the latent image, and repeating the exposing, color-developing and treating steps on said film strip for each of the other two color-separation negatives after each treating step.

2. The process of claim 1 wherein the solution of the bromide and ferricyanide salts are in a ratio of about 10% ferricyanide salt and about 10% bromide salt.

3. The process of claim 1 wherein the bromide salt is potassium bromide.

4. The process of claim 1 wherein the ferricyanide salt is potassium ferricyanide.

5. The process of making a full color photographic print from three color-separation negatives, comprising the steps of: utilizing a film strip comprising a carrier and a single layer black-and-white silver halide emulsion,

exposing the film strip through one of said color-separation negatives to form an image, color-developing the exposed film strip using a dye coupler, treating the color developed film at a temperature between 80° F. and 120° F. with an aqueous solution consisting essentially of about 10% ferricyanide salt and about 10% bromide salt to entirely remove the latent image, repeating the exposing, treating and color-developing steps using a second color-separation negative and dye coupler, exposing the film strip through the third color separation negative, color-developing the exposed film using a third dye coupler without resensitizing said emulsion after either treating step, bleaching the film strip, and fixing.

6. The process of claim 5 wherein the film strip is exposed for a sound track after the second color-developing step.

7. A process of making a full color photographic print containing cyan, magenta and yellow from three color-separation negatives comprising the steps of: utilizing a film strip comprising a carrier and a single layer black-and-white silver halide emulsion, exposing the film strip through one of said color-separation negatives to form an image, color-developing the exposed film strip using the appropriate dye coupler, treating the color developed film strip at a temperature between about 80° F. and about 120° F. with a solution consisting essentially of about 10% bromide salt and about 10% ferricyanide salt to entirely remove the latent image, repeating said exposing, treating and color-developing steps using a second color-separation negative and dye couplers, without resensitizing said emulsion after each treating step, exposing the dyed film strip containing cyan and magenta through the third color-separation negative, color-developing the exposed film strip for yellow using dye coupler means, bleaching the film strip, and fixing.

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J. TRAVIS BROWN, *Primary Examiner.*