Oct. 8, 1935.

W. T. CRESPINEL

2,016,666

COLORED PHOTOGRAPH AND METHOD OF MAKING SAME

Filed Dec. 2, 1932

Fig.1. POSITIVE IMAGE PRINTED FROM LUE COLOR VALUE NEGATIVE Fig.2. R. POSITIVE INAGE PRINTED FROM POSITIVE MAGE PRINTED FROM BLUE COLOR VALUE NEGATIVE RED COLOR VALUE NEGATIVE Fig.3. POSITIVE IMAGE PRINTED FROM RED COLOR VALUE NEGATIVE PRIME IMAGE AAND B REMOVE SURFACE MOISTURE BLEACH IMAGE A CLEAR IMAGE A DYE IMAGE A RED TONE IMAGE A YELLOW THESE STEPS MAY BE COMBINED TONE MAGE B BLUE WASH FILM FIX IMAGE B INVENTOR WILLIAM T. CRESPINEL By Robert M. Fulwider WASH AND DRY FILM

ATTOBNEY

UNITED STATES PATENT OFFICE

2,016,666

COLORED PHOTOGRAPH AND METHOD OF MAKING SAME

William T. Crespinel, Los Angeles, Calif., assignor to Cinecolor Inc., a corporation of California

Application December 2, 1932, Serial No. 645,439

13 Claims. (Cl. 95-2)

My invention relates to the art of color-photography and comprehends the production of a photograph, which will faithfully reproduce substantially all of the colors in the object photo-

- 5 graphed. My new and improved method may be used both in the production of still photographs and in the production of motion pictures in color, although its greatest applicability will be found to be in the latter art for the reason that less
- 10 progress has been made in this field of endeavor than in the former. That being the case I will confine the description of my process, and the film produced thereby, to its application to the production of motion pictures in color, and it will
- 15 therefore be understood that wherever I use the term film I wish to include plates and other photographic media suitable for the reproduction of images.

It is an object of my invention to provide a method of making photographs in color which is 20 comparatively simple in operation and which by reason of its flexibility may be used under various adverse conditions without in any way impairing the quality of the product obtained thereby.

- It is also an object of my invention to provide 25 a method of making photographs in color which is positive and sure in its operation and which does not require constant attention and manipulation of the solutions and equipment, thus mak-
- 30 ing it possible to operate on a large scale with a relatively small number of highly skilled technicians.

A further object of my invention is to produce a colored photograph by the use of only two

- 35 coloring media which will reproduce objects in their natural colors and wherein the colors will have the requisite brilliancy of hue to make the photograph pleasing to the eye.
- Numerous methods of coloring film have been 40 known to the art for some time but so far as I am aware all of these methods are expensive, cumbersome and wasteful. It is therefore another object of my invention to produce a satisfactory colored film at a cost that compares favor-45 ably with the present cost of producing black and
- white film.

Other objects and advantages of my invention will become apparent from the following detailed description of a preferred form of my invention.

In the drawing, Fig. 1 is a representation of a 50 · positive made according to the invention; Fig. 2 is a modification of the positive of Fig. 1; and Fig. 3 is a flow sheet of the process of treating such positives, the process being set forth below 55 in detail.

In the practice of my invention, two colorvalue negatives are produced by any of the well known methods, one of the negatives recording the blue-to-green color-values and the other negative recording the orange-to-red colorvalues of the objects photographed. These negatives may be produced by what is known as a light-splitting camera which divides the light coming through the lens, and passes part of it through a blue-to-green filter onto a sensitive 10 film, while passing the balance of the light through an orange-to-red filter onto a second sensitive film. While the production of the colorvalue negatives forms no part of my invention I will also describe briefly what is known as the 15 Bi-Pack system of producing such negatives, which system I find works admirably in conjunction with my method of producing a colored positive.

The Bi-Pack system as generally known to the 20 art consists in running two negative films, in face to face contact through a standard camera which has the aperture plate slightly modified to accommodate the increased thickness of the two films and which has a special magazine with 25 extra spools therein for the second film. The front film may be what is termed an orthochromatic film, being sensitive to the blue-to-green end of the spectrum only, and is usually provided with a red surface dye on its face. The rear film 30 may be the usual type of panchromatic film. common to the art which records substantially all colors but is predominantly sensitive to the orange-to-red end of the spectrum. When these two films are exposed in the camera the blue- 35 to-green objects are recorded on the front or orthochromatic film and the red objects are recorded on the rear or panchromatic film, the red surface dye on the face of the front film acting as a filter to prevent the passage of any but 40 orange-to-red rays of light to the rear film.

The color-value negatives after exposure, whether obtained by the Bi-Pack, light-splitting or other suitable means are developed, fixed and dried in the usual manner well known in the art 45 and are then ready for use in my invention.

For the positive print I prefer to use a film having an emulsion on each side of the base, this type of film being commercially available by the name of double-coated, or duplitized stock, 50 although by a slight m lification of the process as hereinafter explained I can use a film having either an extra thick emulsion or two standard emulsions on one side of the base. In the practice of the preferred form of my invention I print 55

the negative which has recorded the blue-togreen color values to one side of the positive stock and on the other side of the positive stock I print from the negative which has recorded the orange-

- 5 to-red color values. This printing may be done in any convenient manner so long as accurate registry is had between the respective images of the two negatives. The positive emulsions have incorporated in them a removable light-restrain-
- ing dye which prevents the printing light used 10 in exposing one emulsion from penetrating through the emulsion and base to expose the other emulsion. The two negatives may be printed sir ultaneously or successively depending 15 on the equipment available, and by contact print
 - ing or by projection printing, the particular method used forming no part of my invention. After the negatives have been printed to oppo-
- site sides of the positive, it is developed, fixed and washed in the usual manner and is then ready 20 for coloring. It will be understood that my process belongs to that general class of the color art known as Subtractive Processes wherein a colored image is obtained on the screen by means of filtering out or subtracting certain wave 25
- lengths or colors from white light before it reaches the screen. In the practice of my invention the positive image secured by printing from the orange-to-red color value negative is colored blue-to-green and the positive image printed 30 from the blue-to-green color value negative is
 - colored orange-to-red all in the manner hereinafter specifically disclosed. After printing, developing, and fixing, the posi-
- 35 tive has two sets of silver images thereon, one corresponding to the orange-to-red colors photographed and one corresponding to the blue-togreen colors photographed. These images may be termed black and white in that the free silver is black, shading down to grays with clear or
- 40 white spaces where no light was received by the respective emulsion. The film is now immersed in a solution which we may for descriptive purposes call a priming solution or primer. A suitable formula for such a solution being: 45

Potassium iodide	60	grams
Potassium iodate	2	grams
Pepsin	2	grams
Water	1000	c. c.

The film is allowed to remain in this solution for approximately two minutes or for such additional time as may be necessary to insure all traces of the fixing solution of "Hypo" being 55 removed. Any hypo left in the film when immersed in this priming solution is oxidized to a substance which is easily soluble in water and not detrimental to the subsequent coloring. It is very necessary that the hypo be entirely removed before the subsequent steps for any traces 60 of it remaining will produce irregular and faulty color. The pepsin in this solution in conjunction with the bleach used in the next step insures a fine-grained transparent and well defined image, 65 due to the fact that as pepsin is a protective colloid, it has a tendency to bring the silver iodide formed into a colloidal state instead of a granular one with a consequently finer grained image than could otherwise be obtained. Fur-70 thermore, the pepsin assists the mordanting in that the finer the grain of the image, the more

- complete can be the mordanting action. After removal from the priming solution the
- surface moisture is removed from the film by 75 any convenient means as by air blast or wipers,

Thereupon that side only of the positive which was printed from the blue-to-green color value negative and which is to be colored orange-tored is treated by any convenient means with a bleaching solution, which is also a mordant for basic dyes and which may be made up substantially as follows:

Potassium iodide	50	grams	
Iodine	5	grams	10
Acetic acid	5	grams	10
Sodium acetate	5	grams	
Water	1000	c. c.	

The silver image on the bleached side of the film is converted by the bleach into a silver iodide 15 image which is capable of mordanting basic dyes. The film is then given a brief water wash to remove any excess bleach adhering to the emulsion and is immersed in a clearing solution of potassium metabisulphite and water which can be 20 made up in the proportion of 5 grams of potassium metabisulphite to 1000 c. c. of water. The action of the clearing solution is to convert any free iodine remaining in the emulsion after bleaching, to potassium iodide which is soluble 25 in water and which is then removed by means of another water wash.

At this stage of the process we have a bleached image on one side of the film which is to be colored orange-to-red, and on the other side of 30 the film a free silver image which has remained substantially unchanged and which is to be subsequently colored blue-to-green.

The film is now immersed in a solution of basic dye which will give the desired orange-to- 35 red color to the bleached images. Two suitable dye solutions for this step are as follows:

- (1) Fuchsine chrystals (Shultz 512) _____ 30 c. c. Auromine O (Shultz 493) _____ 70 c. c. 40
- (2) Safranine Y (Shultz 679) 70 c. c. Rhodamine B, extra conc. (Shultz 673)_____ 30 c. c.

Each of the component solutions mentioned 45 above is made up by dissolving 1 gram of solid dye in 100 c. c. of distilled water.

Whenever it becomes necessary to mix dyes to get a resultant color partaking of the individual colors of the respective dyes the inherent problem 50 of constant control of proportions arises. Consequently I have found it advisable in some instances to produce the orange-to-red images by a combination of a single dye and a colored metallic tone. In this variation of my process 55 I prefer to use a dye such as Safranine Y (Shultz 679) which is of a magenta color, and then immerse the film in a weak solution of mercuric nitrate which replaces the colorless silver iodide image with a mercuric iodide image which has a 60 yellow color. The combination of this yellow iodide image with the magenta dyed image gives the desired orange-to-red colors with substantially a yellow in the very thin portions of the 65 image.

Following this step the film is immersed in a blue toning solution a suitable formula for which is as follows:

Ferric ammonium oxalate	6 grams_{70}	
Potassium ferricyanide	6 grams	
Ammonium chloride	10 grams	
Hydrochloric acid (conc.)	5 c. c.	
Water	1000 c. c.	

The free silver images in the unbleached emul- 75

2

50

5

sion are converted by this solution to ferricferrocyanide images which have a blue-to-green color. Some opaque silver ferrocyanide is also formed in this reaction which is removed by subsequent treatment as hereinafter described.

To shorten the time of processing, the step of treating with mercuric nitrate (if that step be used) may be combined with the blue toning operation by merely adding a small amount, say 1

gram, of mercuric nitrate to the blue toning solution made up as before mentioned. When the film is immersed in this combined solution the blue toning constituents do not interfere with the action of the mercuric nitrate on the silver iodide 15 images and the nitrate in no way hinders complete toning of the silver images by the other

constituents of the solution. When the film has remained in the toning solution approximately 2 minutes it is given another

- water wash and the surface moisture removed in any convenient manner. The iron-toned images are then subjected to a weak fixing solution containing for example 4 oz. of sodium thiosulphate to 1000 c. c. of water which removes the white
- 25 silver ferrocyanide from the toned images, leaving a transparent film with a series of blue-togreen images on one side and a series of orangeto-red images on the other side thereof in registry with the respective blue-to-green images.
- 30 After leaving the fixing solution the film is washed and thoroughly dried and is then ready for use. If it is desired to increase the life of the film it may be treated with a transparent varnish to give it a protective coating which will reduce the wear and tear attendant on its being 35

run through projection machines. In many cases for sound motion picture work it is desirable to have a sound track on the positive print. In this case the sound track negative

- is printed to the side of the picture positive that 40 is to be colored blue and is toned blue along with the picture images on that side of the film. If for any reason a black and white sound track is desired the positive track can be varnished im-45 mediately after printing and before coloring, to
- render it unaffected by the subsequent application of the coloring solution.

While I have gone into considerable detail in describing a preferred form of my invention as

- applied to the motion picture art it is to be understood that there are many variations possible in its practice without in any way going outside of its proper scope. As previously mentioned my invention may employ a film having two
- 55 images on the same side of the base, obtained in different levels of an extra thick emulsion or in two superposed emulsions. The only modification of my process necessary to utilize a film of this structure is to regulate the time of immer-
- sion for those steps requiring treatment of one image only. In brief the operations involved in treating such a film would be as follows:

The image to be colored blue-to-green is printed through the base of the positive stock on to the 65 bottom or inner emulsion and the image to be colored orange-to-red is printed to the face of the film on the outer emulsion. The film is then developed fixed and washed as before, and immersed

70 in the priming solution. From the primer it goes to the bleach and is left in this solution just long enough to bleach the outer image without affecting the inner image. In the preferred form of this modification the film is then dyed with a 75 magenta dye and immersed in the blue toning solution containing mercuric nitrate for a length of time sufficient to allow the iron tone to fully convert the inner silver image while the outer dyetoned image is being converted to mercuric iodide to give the resultant orange-to-red color as hereinbefore explained. In the final fixing bath it will be found desirable to add a small quantity of potassium iodide so that there will be no danger of the hypo breaking down the iodide image which has the red dye mordanted thereon. 10

It will be understood that the formulas given are illustrative only, and while I have found the proportions set out to be very successful in my work so far, I recognize that the quantities of the various ingredients may be varied between rather 15 wide limits while still obtaining good color. Likewise there are other chemicals which may be substituted for some of the ingredients of the various solutions used in my preferred form which 20 secure equivalent results.

These and other variations, modifications and equivalents will be evident to those skilled in the art, all of which may be practiced without in any manner falling outside the scope of my inven-9.5 tion.

I claim as my invention:

1. In a colored photograph the combination of: a transparent base; an iron-toned blue image carried by said transparent base; and a mercurytoned yellow image carried by said transparent 30 base and in registry with said first image, said mercury toned yellow image having a magenta basic dye mordanted thereon.

2. In a colored photograph the combination of: a transparent base; an iron toned image carried 85 by said transparent base; a mercury toned image carried by said transparent base and in registry with said iron toned image; and a basic dye mordanted in situ on said mercury toned image.

3. The method of making photographs in color 40 which includes: producing complementary colorvalue images on a film; treating said images with a priming solution: bleaching one of said images with a solution which is also a mordant for basic dyes; treating said film with a solution of basic 45 dye; treating said film with an iron toning solution containing a mercuric salt; and fixing said images to make them transparent.

4. The method of making a colored photograph 50 which includes: producing complementary colorvalue images on opposite sides of a film; treating said images with a priming solution; treating the image on one side only of said film with a solution which will mordant a dye in situ; subjecting said 55 mordanted image to a dye; toning the other of said images while converting said mordanted image to a color complementary to the color of said toned image; fixing said images; and drying said images.

5. The method of making a photograph in color which includes: producing complementary color-value images on a film; converting one of said images to silver iodide; dying said image with s basic dye; toning said second image blue- 65 to-green while converting said silver iodide image to mercuric iodide; and fixing said images.

6. The method of making a photograph in color which includes: producing a plurality of images in registry on a film said images being of 70 different color-values; treating said images with a solution containing pepsin; dye-toning one of said images orange-to-red; and coloring the other of said images blue-to-green.

> 7. The method of making a colored transpar- 75

5

ency which includes: producing a plurality of superposed images on a film; treating said images with a solution containing pepsin; dyeing one of said images; and giving to the second of said 5 images a color substantially complementary to the color of said dyed image.

8. The method of making photographs in color which includes: producing an image on one side of a film; producing an image on the opposite side

10 of said film and in registry with said first image, said second image being of a color value substantially complementary to that of said first image; treating said first image only with an iodide mordant; immersing said film in a solution of
15 magenta basic dye; immersing said film in an iron toning solution to give said second image a blue-to-green color; converting said first image to a mercuric iodide without removing said basic
20 dye; and fixing said images to make them more transparent.

9. In a colored photograph the combination of:
a base; a toned image carried by said base; and a mercury toned image carried by said base in
registry with said first named image, said mer-

cury toned image having a basic dye mordanted thereon.

10. The method of making a photograph in color which includes: producing complementary color-value images on a film in register with each other; converting one of said images to silver iodide; dyeing said image; toning said second image blue to green; and converting said silver iodide image to mercuric iodide.

11. The method of making a photograph in 10 color which includes: producing complementary color-value images on a film; dyetoning one of said images orange to red; mercury toning said image; and toning the other of said images blue to green. 15

12. The step in dye-toning a developed photographic image which consists in treating said developed image with pepsin prior to said dyetoning operation.

13. The method of dye-toning a photographic 20 image which includes: treating said image with a solution containing pepsin; bleaching said image; and submitting said bleached image to the action of a basic dye.

WILLIAM T. CRESPINEL. 25