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COLOR PHOTOGRAPHIC PROCESS

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This invention relates to an improved photographic process for making prints in color by reversal and for making subtractive color photographs. In the preferred form is used a single photographic support coated with a plurality of light sensitive emulsions, each sensitized specifically for a certain portion of the spectrum so as to record one of the component color sensations, at least one of the sensitizing dyes having the property of surviving the successive action of the photographic developer and a chemical solvent for developed silver, and in which the color records are differentially developed and colored by making use of this particular property of at least one of the sensitizing dyes.

It has previously been proposed to employ, in subtractive color processes intended to give a complete color picture by a single exposure in an ordinary camera, and subsequent development and differential coloring of the component color records, a photographic support bearing a plurality of light sensitive emulsions separately sensitized for different regions of the spectrum, either in superposed layers as mixed droplets or as mixed grains. One difficulty in the operation of such processes lies in the tendency of the usual photographic sensitizers for different regions of the spectrum to diffuse from one emulsion layer, droplet, or grain to another, thereby sensitizing a large number of the grains for all regions of the spectrum, and thus preventing a sharp separation of the component color records in the primary exposure to a light image. A second difficulty was the fact that the red sensitizing dyes previously used were not especially specific for the red region of the spectrum; that is, they did not have a well defined minimum in the green. A third difficulty lies in differentially developing and coloring the component record so as to obtain a subtractive color negative or positive while submitting the photographic member as a unit to the same solutions, light exposures, and other steps in the process.

I have found means for overcoming these difficulties by the use of certain known optical sensitizers for silver halides together with certain processing steps which can be successfully carried out as a result of the use of these dyes.

I have found that certain sensitizing dyes are much more resistant to diffusion from one photographic emulsion layer to another in immediate contact therewith than other sensitizing dyes. Dyes which have this property, together with the property of sensitizing preponderantly in the red region of the spectrum, are the neo-thiazolo carbocyanines described in applications Serial Nos. 548,025 and 548,026 filed June 30, 1931, by L. G. S. Brooker and the aryl substituted dibenzo thio carbocyanines disclosed in applications Serial Nos. 435,104 and 435,105 filed March 12, 1930, by the same inventor. Particularly useful examples are, of the first class, 4.4′ diphenyl 3.3′ diethyl 7-(4 phenyl thiazole ethiodide) methyl thiazolo carbocyanine iodide, hereinafter referred to as dye 555, and, of the second class, 2:2′ dimethyl 8 phenyl 3:4, 3′:4′ dibenzo thio carbocyanine iodide, hereinafter referred to as dye 666. Silver bromide sensitized with one or the other of these dyes shows a distinct maximum of sensitivity in the red region and a distinct minimum in the green. A dye which combines the antidiffusing property with sensitizing specifically for the green region of the spectrum is 1′, 2-diethyl-3, 4-benzo-thio-pseudo-cyanine-iodide (hereinafter referred to as dye 777). The last named is described in co-pending applications Nos. 435,105 and 437,017 filed March 12, 1930 and March 19, 1930, respectively, by L. G. S. Brooker.

I have also found that dye 777 has another property which enables certain useful steps to be carried out successfully in the differential development and coloring of the component color records. This property is the ability to retain its optical sensitizing power for a subsequent light exposure after the successive action of a photographic developer and of a chemical solvent for silver such as an acid bichromate solution. Other dyes which I have found to possess this property are rhodamine 6G and erythrosin. This property is not possessed by the majority of

sensitizing dyes, which are greatly altered or destroyed by the action of dilute acids or of oxidizing agents.

In my invention, I therefore make use of these specific properties of certain dyes and by their use I am able to successfully perform certain operations which have hitherto been unsuccessful. The following specific examples illustrate my invention.

Two silver bromide emulsions are sensitized, respectively, with suitable red and green sensitizers resistant to diffusion. This resistance to diffusion may be due to the colloidal dimensions of the dye particles, making them non-dialyzable, to the firmness of the adsorption of the dye to the silver halide grains, to the extreme insolubility of the dye in water or to any combination of these properties. No restriction with regard to the cause of the resistance to diffusion is here intended. Suitable dyes of this kind are dye 555 or dye 666 as red sensitizers, and dye 777 as a green sensitizer. One or both of the sensitizers must be of the type that survives the consecutive action of a photographic developer and a chemical solvent for silver. Of the dyes just mentioned dye 777 is of this type. These two emulsions may be then coated on a single support in any one of the four following ways:

1.—The emulsions may be mixed and coated as a layer of heterogeneous spectral sensitivity as regards the individual grains.

2.—The emulsions may be atomized, mixed and coated as a layer of heterogeneous spectral sensitivity as regards the constituent droplets.

3.—The emulsions may be coated as separate superposed layers of different spectral sensitivity on the same side of a common support.

4.—The emulsions may be coated on opposite sides of a common support, which should be as thin as possible.

It is obvious that where the differentially sensitized particles or emulsions are in contact it is essential that the dyes shall not diffuse from one to the other. Where, however, the differentially sensitized layers are on opposite sides of the support this is not essential and dyes may be used which have a tendency to diffuse. Such dyes, useful in sensitizing for green, are erythrosin or rhodamin 6G.

The film thus prepared is given a single exposure in an ordinary camera through a yellow filter which absorbs the blue-violet rays to which both emulsions are sensitive. If the film is of the type with separate layers and different sensitivity, the light first passes preferably through the green sensitive layer.

The film is now developed in an ordinary developer.

After washing, the film is immersed in the following solution for a sufficient time to remove the developed negative silver image:

Potassium bichromate	2 grams
Sulphuric acid, concentrated	2 c. c.
Water to	1 liter

After another washing, the film is bathed for a few minutes in a ½% solution of sodium sulphite, which acts as a chemical sensitizer to restore sensitivity to the halide grains.

The film is now exposed to light of a color which will affect the remaining silver halide grains of only one of the photographic emulsions. In the event that both the red and green sensitizers have survived at this stage in the process, the exposure may be to either red or green light. If only one of the sensitizers has survived, the exposure may be to light of a color for which the surviving dye sensitizers, or to yellow light (that is, white light minus blue-violet).

The film is now given a second development either in an ordinary developer or in a color-forming developer. This constitutes, of course, a reversal process.

At this point, there are present in the film a positive image in silver bromide representing the values of one color in the subject and a positive image in silver representing the values of another color in the subject. In the event that the second development was carried out in a color developer, there is also a color image associated with a silver image representing the values of the same color as that represented by the silver image. The color developer is so chosen that the color it forms is complementary to the color whose value it represents, according to the well-known subtractive principle.

Since, now, the two sets of color values are present in different chemical substances, it is possible to transform one or both of these images into suitable color images by well-known chemical operations, of which the following are examples:

1.—The silver bromide image may be converted into one of silver iodide by treatment with potassium iodide, a basic dye or mixture of dyes such as brilliant green, fuchsin, auramine, or rhodamine 6G mordanted thereto, and the silver image toned to a color complementary to that of the dyed image by means of uranium or iron toning solutions or the like. This procedure assumes that an ordinary developer has been used for the second development.

2.—If a color developer has been used for the second development, the silver bromide image may now be exposed to light and developed in another color developer, and the silver images removed with suitable reagents, such as Farmer's reducer, or a ferricyanide-bromide solution followed by plain hypo.

As stated above, it is not necessary that all of the sensitizing dyes survive the first developer and bleaching bath. For example, in a two-color process, it is sufficient for only one to survive. The color sensitizing effect of one dye, say the red sensitized one, may be destroyed by dilute acid bichromate solution but the color sensitizing effect of the other, say dye 777, survives the action of such a bath. Thus, after a bath of dilute sodium sulphite, the green sensitive silver halide grains remaining in the film may be readily developable by exposure to green or yellow light.

It will be seen that although the component color records in the film are differentially colored according to my invention, this differential treatment does not require any mechanical or other external selection of the parts of the film to be treated, but is automatic and depends upon the inherent characteristics of the film and the nature of the various chemical reactions and light exposures to which the entire film is submitted.

In the foregoing specification and the claim the terms "optical sensitizing" and "chemical sensitizing" are used with the usual meanings now common in the art. An optical sensitizer is one which confers, as a rule, added sensitivity to a silver grain by changing its light absorption, and it therefore generally confers sensitivity to spectral regions not previously present. A chemical sensitizer, on the other hand, is one which increases the general sensitivity, restores sensitivity, or confers sensitivity not previously possessed. This is accomplished by intricate changes of a chemical nature concerning which many theories have recently been proposed. It is distinguished from an optical sensitizer in that it is not concerned with a mere change in the light absorption of the grain and therefore, as a rule, does not affect its color sensitivity.

It should be understood that my invention is not restricted by the particular examples given, but that numerous modifications of the outlined procedure may be employed, all of which I consider as included in my invention as expressed by the appended claims.

What I claim is:

1. A photographic reversal process which comprises optically sensitizing a silver halide emulsion layer with a substance such that the silver halide remains differentially color sensitive after the successive actions of a photographic developer and of a chemical solvent for the silver image, exposing said layer to a light image, developing a silver image therein in an ordinary photographic developer, removing the silver image by means of a chemical solvent for said image, chemically sensitizing the remaining silver halide, thereafter exposing the layer to light of that color which renders said optically sensitized silver halide developable, and redeveloping in a second photographic developing bath to produce a positive image.

2. In a photographic process, the steps which comprise optically sensitizing a silver halide emulsion with 1′, 2 diethyl 3,4 benzo thio pseudo cyanine iodide, exposing said emulsion to a light image, submitting said emulsion to the action of a developing agent thereby forming a silver image therein and to a suitable solvent for silver, chemically sensitizing the remaining silver halide, and then exposing the emulsion to green light to which said silver halide is optically sensitized.

3. A photographic reversal process which comprises optically sensitizing a silver halide emulsion with 1′, 2 diethyl 3,4 benzo thio pseudo cyanine iodide, exposing said emulsion to a light image, developing a silver image therein in an ordinary photographic developer, removing the silver image by means of a chemical solvent for said image, chemically sensitizing the remaining silver halide, rendering the remaining chemically and optically sensitized silver halide developable by exposure to light of a color which renders only said optically sensitized silver halide developable and redeveloping in a second photographic developing bath to produce a positive image.

4. A photographic reversal process which comprises optically sensitizing a silver halide emulsion with 1′2 diethyl 3,4 benzothiopseudo cyanine iodide, exposing said emulson to a light image, developing a silver image in an ordinary photographic developer, removing the silver image by means of a chemical solvent for said image, and then chemically sensitizing the remaining silver halide with a dilute solution of sodium bisulphite, thus rendering the remaining chemically and optically sensitized silver halide developable by exposure to light of a color which renders only said optically sensitized silver halide developable.

5. A color photographic process which comprises exposing in a camera a sensitive element comprising two silver halide emulsions sensitized for different colors, at least one of which is optically sensitized with a substance such that the slver halide remains optically sensitized after the action of a photographic developing agent and of a chemical solvent for the silver image, developing a silver image in said element, submitting the element to the action of a bichromate bleaching bath, thereafter exposing the element to light of a color which affects the remaining portions of only one of said emulsions, redeveloping, and then transforming into suitable color images the silver and silver bromide images representing respectively the values of two separate colors.

6. A color photographic process which

comprises exposing in a camera a sensitive element comprising two silver halide emulsions sensitized for different colors, at least one of which is optically sensitized with a substance such that the silver halide remains optically sensitized after the action of a photographic developing agent and of a chemical solvent for the silver image, developing silver images in said element, submitting the element to the action of a bichromate bleaching bath, exposing the element uniformly to light of a color which affects the remaining portions of only one of said emulsions, redeveloping, and then transforming into suitable color images the silver and silver bromide images representing respectively the values of two separate colors.

7. A color photographic process which comprises exposing in a camera a sensitive element comprising two silver halide emulsions sensitized for different colors, at least one of which is optically sensitized with a substance such that the silver halide remains optically sensitized after the action of a photographic developing agent and of a chemical solvent for the silver image, developing silver images in said element, submitting the element to the action of a bichromate bleaching bath, chemically sensitizing the remaining silver halide, exposing the element uniformly to light of a color which affects the remaining portions of only one of said emulsions, redeveloping, and then transforming into suitable color images the silver bromide images representing respectively the values of two separate colors.

8. A color photographic process which comprises exposing in a camera a sensitive element comprising two silver halide emulsions sensitized for different colors, at least one of which is optically sensitized with a substance such that the silver halide remains optically sensitized after the action of a photographic developing agent and of a chemical solvent for the silver image, developing silver images in said element, submitting the element to the action of a bichromate bleaching bath, chemically sensitizing remaining silver halide with a dilute solution of sodium bisulphite, exposing the element uniformly to light of a color which affects the remaining portions of only one of said emulsions, redeveloping, and then transforming into suitable color images the silver and silver bromide images representing respectively the values of two separate colors.

9. A color photographic process which comprises exposing in a camera a sensitive element comprising two silver halide emulsions sensitized for different colors, at least one of which is optically sensitized with a substance such that the silver halide remains optically sensitized after the action of a photographic developing agent and of a chemical solvent for the silver image, developing silver images in said element, submitting the element to the action of a bichromate bleaching bath, chemically sensitizing the remaining silver halide with a dilute solution of sodium bisulphite, exposing the element uniformly to light of a color which affects the remaining portions of only one of said emulsions, redeveloping, and then transforming into suitable color images the silver and silver bromide images representing respectively the values of two separate colors by converting the silver bromide into silver iodide with a solution of potassium iodide, mordanting thereto a blue green basic dye and toning the silver image with a red toning solution.

10. A color photographic process which comprises exposing in a camera a sensitive element comprising two silver halide emulsions sensitized for different colors, at least one of which is optically sensitized with a substance such that the silver halide remains optically sensitized after the action of a photographic developing agent and of a chemical solvent for the silver image, developing said element, submitting the element to the action of a bichromate bleaching bath, chemically sensitizing remaining silver halide with a dilute solution of sodium bisulphite, exposing the element uniformly to light of a color which affects the remaining portions of only one of said emulsions, redeveloping in a color forming developer, reexposing remaining silver bromide uniformly to light, developing said remaining silver bromide in a color forming developer yielding an image complementary in color to that of the first color forming developer, and removing the silver images with suitable reagents.

11. A color photographic process which comprises exposing in a camera a sensitive element comprising a support having a coating of a silver halide emulsion sensitized with a non-diffusing basic green sensitizing dye whose sensitizing properties are retained after the action of a photographic developing agent and of a chemical solvent for silver and another coating of silver halide emulsion sensitized with a non-diffusing red sensitizing dye, developing said element, submitting the element to the action of a bichromate bleaching bath, chemically sensitizing remaining silver halide with a dilute solution of sodium bisulphite, exposing the element uniformly to light of a color which affects the remaining portions of only one of said emulsions, redeveloping, and then transforming into suitable color images the silver and silver bromide images representing respectively the values of two separate colors by converting the silver bromide into silver iodide with a solution of potassium iodide, mordanting thereto a blue green basic dye

and toning the silver image with a red toning solution.

12. A color photographic process which comprises exposing in a camera a sensitive element comprising a support having a coating of a silver halide emulsion sensitized with 1',2 diethyl 3,4 benzo thio pseudo cyanine iodide and another coating of a silver halide emulsion sensitized with 4,4' diphenyl 3,3' diethyl 7-(4 phenyl thiazole ethiodide) methyl thiazolo carbocyanine iodide, developing said element, submitting the element to the action of a bichromate bleaching bath, chemically sensitizing remaining silver halide with a dilute solution of sodium bisulphite, exposing the element uniformly to light of a color which affects the remaining portions of only one of said emulsions, redeveloping, and then transforming into suitable color images the silver and silver bromide images representing respectively the values of two separate colors by converting the silver bromide into silver iodide with a solution of potassium iodide, mordanting thereto a blue green basic dye and toning the silver image with a red toning solution.

13. A color photographic process which comprises exposing in a camera a sensitive element comprising a support coated with two silver halide emulsions, one of which is sensitized with 1',2 diethyl 3,4 benzo thio pseudo cyanine iodide and the other of which is sensitized with a red sensitizing dye, developing said element, submitting the element to the action of a bichromate bleaching bath, chemically sensitizing the remaining silver halide, exposing the element uniformly to light of a color which affects the remaining portions of only one of said emulsions, re-developing and then transforming into suitable color images the silver and silver bromide images representing respectively the values of two separate colors.

14. A color photographic process which comprises exposing in a camera a sensitive element comprising a support coated with two superposed silver halide emulsions, one of which is sensitized with 1',2 diethyl 3,4 benzo thio pseudo cyanine iodide and the other of which is sensitized with a specific red sensitizing dye, developing said element submitting the element to the action of a bichromate bleaching bath, chemically sensitizing the remaining silver halide, exposing the element uniformly to light of a color which affects the remaining portions of only one of said emulsions, re-developing and then transforming into suitable color images the silver and silver bromide images representing respectively the values of two separate colors.

15. A color photographic process which comprises exposing in a camera a sensitive element comprising a support coated with two silver halide emulsions, one of which is sensitized with 1,2 diethyl 3,4 benzo thio pseudo cyanine iodide and the other of which is sensitized with a non-diffusing specific red sensitizing dye, developing said element, submitting the element to the action of a bichromate bleaching bath, chemically sensitizing the remaining silver halide, exposing the element uniformly to light of a color which affects the remaining portions of only one of said emulsions, re-developing, and then transforming into suitable color images the silver and silver bromide images representing respectively the values of two separate colors.

16. A color photographic process which comprises exposing in a camera a sensitive element comprising a support coated with two superposed silver halide emulsions, one of which is sensitized with 1',2 diethyl 3,4 benzo thio pseudo cyanine iodide and the other of which is sensitized with 4,4' diphenyl 3,3' dithyl 7-(4 phenyl thiazole ethiodide) methyl thiazolo carbocyanine iodide, developing said element, submitting the element to the action of a bichromate bleaching bath, chemically sensitizing the remaining silver halide, exposing the element uniformly to light of a color which affects the remaining portions of only one of said emulsions, re-developing, and then transforming into suitable color images the silver and silver bromide images representing respectively the values of two separate colors.

17. A color photographic process which comprises exposing in a camera a sensitive element comprising a support coated with two superposed silver halide emulsions, one of which is sensitized with 1',2 diethyl 3,4 benzo thio pseudo cyanine iodide and the other of which is sensitized with 4,4' diphenyl 3,3' diethyl 7-(4 phenyl thiazole ethiodide) methyl thiazole carbocyanine iodide, developing said element, submitting the element to the action of a bichromate bleaching bath, chemically sensitizing the remaining silver halide, exposing the element uniformly to light of a color which affects the remaining portions of only one of said emulsions, re-developing, and then transforming into suitable color images the silver and silver bromide images representing respectively the values of two separate colors by converting the silver bromide into silver iodide with a solution of potassium iodide, mordanting thereto a blue green basic dye, and toning the silver image with a red toning solution.

Signed at Rochester, New York this 18th day of August 1931.

MERRILL W. SEYMOUR.