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COLOR PHOTOGRAPHIC MATERIAL

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This invention relates to a material useful in color reversal processes and particularly in making subtractive color photographs. In the preferred form, a single photographic support is 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 lay 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 larger 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 lay in differentially developing and coloring the component records 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-thiazole carbocyanies 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 thiazole 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 anti-diffusing 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 copending applications 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. These may be successfully used in carrying out certain forms of my invention. This prop-

erty 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 are then coated on a single support in 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 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 rhodamine 6G.

The sensitized products above described are useful in various photographic reversal and color processes, particularly those described in my application filed concurrently herewith.

It is to be understood that I contemplate, as included within my invention, all such modifications and equivalents as fall within the scope of the appended claims.

What I claim is:

1. A sensitive photographic element for the production of color photographs comprising a support carrying in layer form a plurality of silver halide emulsions sensitized for different colors, one of which is optically sensitized with a salt of 1',2-diethyl-3,4-benzothiopseudo cyanine.

2. A sensitive photographic element for the production of color photographs comprising a support carrying in layer form a plurality of silver halide emulsions sensitized for different colors, one of which is optically sensitized with 1',2-diethyl-3,4-benzothiopseudo cyanine iodide.

3. A sensitive photographic element for the production of color photographs comprising a support carrying in layer form a plurality of superposed silver halide emulsions sensitized for different colors, one of which is optically sensitized with 1',2-diethyl-3,4-benzothiopseudo cyanine iodide.

4. A sensitive photographic element for the production of color photographs comprising a support carrying in layer form a plurality of mixed silver halide emulsions sensitized for different colors, one of which is optically sensitized with 1',2-diethyl-3,4-benzothiopseudo cyanine iodide.

5. A film for the production of color photographs which comprises a support, on one face of said support a silver halide emulsion sensitized with 1',2-diethyl-3,4-benzothiopseudo cyanine iodide, and on the other face of said support a silver halide emulsion sensitized with a specific red sensitizing dye having a well defined minimum sensitizing action in the green.

6. A film for the production of color photographs which comprises a support, on one face of said support a silver halide emulsion sensitized with 1',2-diethyl-3,4-benzothiopseudo cyanine iodide, and on the other face of said support a silver halide emulsion sensitized with a non-diffusing specific red sensitizing dye having a well defined minimum sensitizing action in the green.

7. A film for the production of color photographs which comprises a support, on one face of said support a silver halide emulsion sensitized with 1',2-diethyl-3,4-benzothiopseudo cyanine iodide and on the other face of said support a silver halide emulsion sensitized with 4.4'-diphenyl-3,3'-diethyl 7-(4 phenyl thiazole ethiodide) methyl thiazole carbocyanine iodide.

8. A film for the production of color photographs which comprises a support, and two superposed silver halide emulsions, one of which is sensitized with 1',2-diethyl-3,4-benzothiopseudo cyanine iodide, and the other of which is sensitized with a non-diffusing specific red sensitizing dye having a well defined minimum sensitizing action in the green.

9. A film for the production of color photographs which comprises a support, and two superposed silver halide emulsions, one of

which is sensitized with 1',2-diethyl-3,4-benzothiopseudo 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.

10. A film for the production of color photographs which comprises a support, and coated on one face of said support a sensitive layer consisting of a mixture of two separately color sensitized emulsions, one of said emulsions being sensitized with 1',2-diethyl-3,4-benzothiopseudo cyanine iodide, and the other of said emulsions being sensitized with a non-diffusing specific red sensitizing dye having a well defined minimum sensitizing action in the green.

11. A film for the production of color photographs which comprises a support, and coated on one face of said support a sensitive layer consisting of a mixture of two separately color sensitized emulsions, one of said emulsions being sensitized with 1',2-diethyl-3,4-benzothiopseudo cyanine iodide and the other of said emulsions being sensitized with 4,4'-diphenyl-3,3'-diethyl 7-(4 phenyl thiazole ethiodide) methyl thiazole carbocyanine iodide.

Signed at Rochester, New York, this 20th day of August 1931.

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