

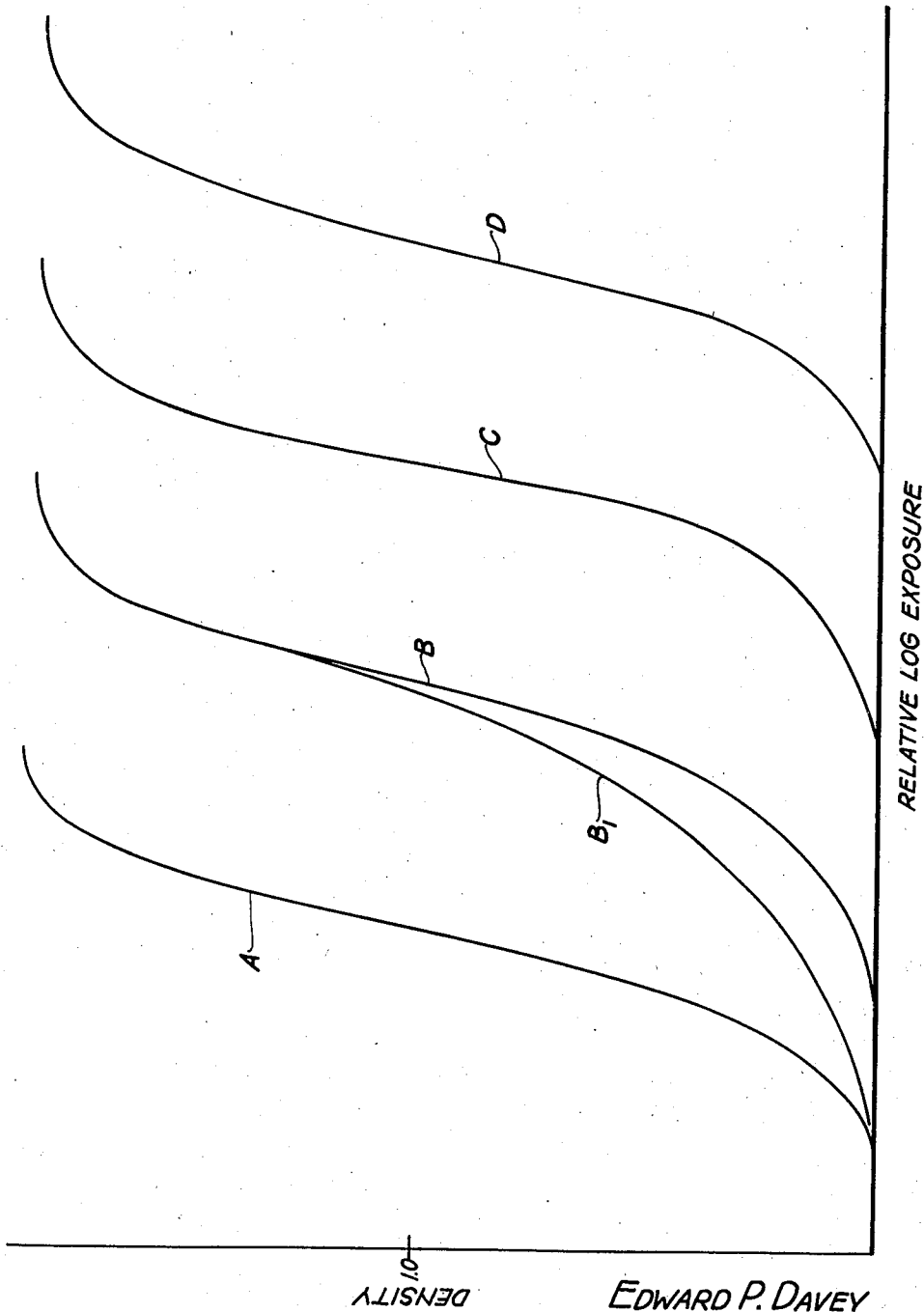
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DIFFUSION OF SENSITIZING DYES IN PHOTOGRAPHIC EMULSIONS

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DIFFUSION OF SENSITIZING DYES IN
PHOTOGRAPHIC EMULSIONS

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This invention relates to the retardation of diffusion of sensitizing dyes in photographic emulsions.

For certain purposes in photography there are required sensitive papers, films, plates and similar materials comprising two or more emulsions which respond in different ways to differently colored light. Thus, one of the emulsions may be insensitive to light of a color to which a second emulsion may be sensitive. In the production of these sensitive materials, the emulsions are sometimes mixed before application to the support, while in other instances the emulsions are applied successively in layers to the support. For example, it is common practice in the production of sensitive materials for use in color photography to apply successively to the support layers of emulsions sensitive to different regions of the spectrum. In certain instances in color photographic elements, two or more emulsions are mixed together in one layer.

As a further example of the use of sensitive materials comprising two or more emulsions which respond in different ways to differently colored light may be mentioned printing papers which are capable of giving a result of high or low contrast, depending upon the color of the light used in printing. Such papers can be produced by applying to a paper support a mixture of two emulsions, one of which gives an image of high contrast and can be printed by using light of one color, and the second gives an image of low contrast and can be printed by using a light of a different color. Instead of a mixture of two emulsions, the emulsions can be applied successively to the paper support. The emulsions used in such printing papers, or in the aforementioned color photographic materials, may be all of one type, say silver chloride or silver bromide, or the emulsions may be of different types.

Whether the emulsions are of the same or of different types, the different sensitivity of the emulsions to differently colored light can be controlled by means of sensitizing dyes. Thus one emulsion may be prepared free from sensitizing dye and, hence, sensitive to blue light but not to light of longer wavelengths, while the other emulsion may contain a dye which sensitizes the emulsion to yellow light, in which case the second emulsion will be sensitive both to yellow and to blue light, since the emulsion possesses a natural sensitivity to blue. Alternatively the two emulsions may contain different sensitizing dyes,

so that each emulsion is dye-sensitized for a different spectral region.

Numerous sensitizing dyes which may be employed are known, including among others sensitizing dyes from the cyanine, the hemicyanine, the merocyanine, the oxonol and the hemioxonol dye classes. In practice, however, the sensitizing dye or dyes adsorbed on the grains of one emulsion have a greater or lesser tendency to wander or diffuse to the grains of another emulsion where the dye is not desired. If such diffusion occurs, the initial difference in sensitivity between the emulsions is, of course, reduced, and may even be lost practically entirely. Even where the emulsions are applied in consecutive layers, the tendency of certain dyes to wander from one layer to another is very marked. Only a relatively few of the well-known powerful sensitizing dyes have a low enough resistance to wander to be useful in the production of photographic materials of the kind described above.

To reduce this undesirable tendency to wander, it has been proposed to introduce into the molecules of the sensitizing dyes, long-chain organic groups. Dye molecules containing such chains show a lesser tendency to diffuse, but such dyes also show a greater or lesser decrease in sensitizing power, depending upon the point of attachment of the long-chain organic group. At best, such a method of retarding diffusion is at the expense of sensitizing power. It has also been proposed to retard wandering of quaternary salt types of sensitizing dyes in photographic emulsions by incorporating perchlorates, such as sodium perchlorate, in the emulsions containing the dyes. However, this method leaves much to be desired, and in the case of non-quaternary salt types of dyes, such as merocyanine dyes, the method is of no utility whatsoever.

It is, accordingly, an object of my invention to provide a process for retarding diffusion of sensitizing dyes. Another object is to provide emulsions containing sensitizing dyes which are retarded from diffusion. Other objects will become apparent hereinafter.

I have found that diffusion or wandering of sensitizing dyes in photographic gelatino-silver-halide emulsions can be retarded by dispersing a substantially water-insoluble organic colloid in the emulsion not earlier than the sensitizing dye is dispersed in the emulsion. Advantageously, the water-insoluble organic colloid and the sensitizing dye are dispersed in the emulsion simultaneously, or the water-insoluble organic colloid is dispersed in the emulsion immediately after

the sensitizing dye. If the water-insoluble colloid is incorporated in the emulsion before the sensitizing dye, poor sensitization will result.

As substantially water-insoluble organic colloids, water-insoluble resins are exemplary. Examples of substantially water-insoluble resins are: whole shellac, hard shellac, soft shellac, hydrolyzed soft shellac, colophony, synthetic glyptal resins, gum mastic, dammar, sandarach, copal, kauri and coumarone resins. Substantially water-insoluble cellulose derivatives, such as substantially water-insoluble cellulose esters, e. g., acetate, and cellulose ethers, are further examples of substantially water-insoluble organic colloids. The resins, however, especially the shellacs, are advantageously employed in practicing my invention.

It is, of course, well known that sensitizing dyes are advantageously incorporated in photographic silver halide emulsions in the form of solutions in organic solvents, such as methyl alcohol, ethyl alcohol, acetone, etc. I have found that the water-insoluble organic colloid is also advantageously incorporated in the emulsions in the form of a solution in an organic solvent. Where possible, the same solvent is advantageously employed for both the dye and the water-insoluble colloid. It is advantageous to reduce the volume of the solvent as far as is compatible with efficient sensitizing and proper dispersion of the colloid in the emulsion. The colloid being substantially water insoluble, of course, precipitates as a fine dispersion when a solution of it is added to the emulsion. If too little solvent is used the colloid coagulates or gives a coarse suspension. On the other hand, excessive amounts of solvents which are capable of dissolving the sensitizing dyes should be avoided, as they act to promote diffusion of the sensitizing dyes in the emulsions.

To illustrate how diffusion of a typical sensitizing dye is accomplished in accordance with my invention, I will refer to a mixture of about 70% of a high contrast chloride emulsion sensitized to the green with 5-[2-ethyl-2(3)-benzoxazolyldene]ethylidene]-3-ethyl-1-phenyl-2-thiohydantoin, and about 30% of a soft bromide emulsion. Both the chloride and the bromide emulsion contain silver halide in a concentration equal to about 200 grams of silver nitrate per 7.5 liters of emulsion.

In the accompanying drawing are depicted sensitometric curves for such a mixed emulsion, exposed through a yellow (Wratten No. 5) filter, so that only the contrasty component responds to the illumination, unless wandering of the sensitizing dye occurs. If wandering or diffusion occurs, a toe will be given to the curve, owing to admixture of the faster soft bromide emulsion.

Curve A is the sensitometric curve for the contrasty chloride emulsion sensitized with the above green sensitizer in a concentration of 100 mg. per 7.5 liters of emulsion, the sensitizing dye having been incorporated in the emulsion along with ethyl alcohol in a concentration equal to 200 cc. per 7.5 liters of emulsion.

Curve B is the sensitometric curve for the mixed emulsion (70% of the contrasty chloride emulsion sensitized as indicated above, mixed with 30% of the soft bromide emulsion, coated and exposed immediately after mixing). The elongated toe of this curve relative to curve A is apparent, indicating that wandering of the sensitizing dye has occurred. Curve B₁ is the sensitometric curve for the same mixed emulsion,

after standing for about 20 minutes. Wandering is now very marked.

Curve C is the sensitometric curve for the same mixed emulsion represented by curves B and B₁, except that before mixing the two emulsions; the chloride emulsion was treated with soft shellac in a concentration of 30 grams per 7.5 liters of emulsion, using ethyl alcohol as a solvent for the lac in a concentration of 500 cc. per 7.5 liters of emulsion. The longer straight line portion of this curve as compared with curves B and B₁ indicates a retardation of wandering of the sensitizing dye.

Curve D is the sensitometric curve for the same mixed emulsion represented by curve C, except that the solvent for the sensitizing dye was cut to 133 cc. per 7.5 liters of emulsion and the solvent for the lac was cut to 333 cc. per 7.5 liters of emulsion, and soft lac was also added to the bromide emulsion in a concentration of 30 grams per 7.5 liters of emulsion, using 333 cc. of ethyl alcohol to dissolve the lac. This curve is nearly equal to curve A, indicating substantially no diffusion of the sensitizing dye.

The above emulsion represented by curve D is especially well suited for the production of variable contrast photographic printing papers, since by exposure through appropriate filters different contrasts can be obtained under the same conditions of development. Soft shellac is especially well suited to accomplish non-diffusion. Glyptal resins and gum mastic are also well suited. The resin usually imparts a matte appearance to the paper print, but the print can be glazed, and then gives a glossy surface in the ordinary way.

Similar emulsions were prepared where the sensitizing dye employed was 2,3'-diethyl-3,4-benzoxathiazolinocarbocyanine iodide or 2,2'-diethyloxacarbocyanine iodide instead of the thiohydantoin compound indicated above, and the water-insoluble organic colloid, especially the soft shellac resin, substantially retarded diffusion of the sensitizing dye.

A mixed emulsion such as might be employed in a color photographic element was also prepared with some of the silver halide grains sensitized to the blue with 1-methyl-1'-ethyl-2,2'-azacyanine iodide, and some of the grains sensitized to the red with 3-ethyl-5-[2-ethyl-1(2)-benzoselenazolyldene]-butenylidene]-1-phenyl-2-thiohydantoin. Diffusion of the sensitizing materials was substantially retarded with soft shellac resin.

The quantity of substantially water-insoluble organic colloid which is most suited to retard diffusion will, of course, depend somewhat upon the sensitizing dye employed and upon the silver halide emulsion employed. In general from about 10 to about 35 grams of water-insoluble colloid for each gram-mole of silver halide will suffice. The total volume of solvent employed for the sensitizing dye and for the water-insoluble colloid is advantageously not more than about 10% of the volume of the emulsion being treated.

What I claim as my invention and desire to be secured by Letters Patent of the United States is:

1. A process for preparing a dye-sensitized mixed-grain photographic silver halide emulsion in which diffusion of the sensitizing dye is retarded comprising incorporating a substantially water-insoluble organic colloid in a photographic silver halide emulsion which contains a sensitizing dye, and then combining the emulsion with another photographic silver halide emulsion se-

lected from the group consisting of those devoid of sensitizing dyes and those containing a sensitizing dye, the diffusion of which has been retarded by incorporating a substantially water-insoluble organic colloid in the emulsion containing the sensitizing dye.

2. A process for preparing a dye-sensitized mixed-grain photographic silver halide emulsion in which diffusion of the sensitizing dye is retarded comprising incorporating a substantially water-insoluble organic colloid in a photographic silver halide emulsion which contains a sensitizing dye, and then combining the emulsion with another photographic silver halide emulsion which is devoid of sensitizing dyes.

3. A process for preparing a dye-sensitized mixed-grain variable contrast photographic silver halide emulsion in which the diffusion of the sensitizing dye is retarded comprising incorporating a substantially water-insoluble organic colloid in a photographic silver halide emulsion which contains a sensitizing dye, and then mixing the emulsion with another photographic silver halide emulsion which differs in contrast from the first emulsion and which is devoid of sensitizing dyes.

4. A process for preparing a dye-sensitized mixed-grain photographic silver halide emulsion in which diffusion of the sensitizing dye is retarded comprising incorporating a substantially water-insoluble resin in a photographic silver halide emulsion which contains a sensitizing dye, and then combining the emulsion with another photographic silver halide emulsion selected from the group consisting of those devoid of sensitizing dyes and those containing a sensitizing dye, the diffusion of which has been retarded by incorporating a substantially water-insoluble resin in the emulsion containing the sensitizing dye.

5. A process for preparing a dye-sensitized mixed-grain variable contrast photographic silver halide emulsion in which diffusion of the sensitizing dye is retarded comprising incorporating a substantially water-insoluble resin in a photographic silver halide emulsion which contains a sensitizing dye, and then combining the emulsion with another photographic silver halide emulsion which differs in contrast from the first emulsion and which is devoid of sensitizing dyes.

6. A process for preparing a dye-sensitized mixed-grain photographic silver halide emulsion in which diffusion of the sensitizing dye is retarded comprising incorporating in a photographic silver halide emulsion which contains a sensitizing dye from about 15 to about 35 grams for each gram-mole of silver halide in the emulsion a substantially water-insoluble organic colloid, and then combining the emulsion with another photographic silver halide emulsion selected from the group consisting of those devoid of sensitizing dyes and those containing a sensitizing dye, the diffusion of which has been retarded by incorporating in the emulsion containing the sensitizing dye from about 15 to about 35 grams for each gram-mole of silver halide in the emulsion, a substantially water-insoluble organic colloid.

7. A process for preparing a dye-sensitized mixed-grain variable contrast photographic silver halide emulsion in which diffusion of the sensitizing dye is retarded comprising incorporating in a photographic silver halide emulsion which contains a sensitizing dye from about 15 to about 35 grams for each gram-mole of silver halide in the emulsion, a substantially water-

insoluble organic colloid, and then combining the emulsion with another photographic silver halide emulsion which differs in contrast from the first emulsion and which is devoid of sensitizing dyes.

8. A process for preparing a dye-sensitized mixed-grain photographic silver halide emulsion in which diffusion of the sensitizing dye is retarded comprising incorporating in a photographic silver halide emulsion which contains a sensitizing dye soft shellac, and then combining the emulsion with another photographic silver halide emulsion selected from the group consisting of those devoid of sensitizing dyes and those containing a sensitizing dye, the diffusion of which has been retarded by incorporating, in the emulsion containing the sensitizing dye, soft shellac.

9. A process for preparing a dye-sensitized mixed-grain variable contrast photographic silver halide emulsion in which diffusion of the sensitizing dye is retarded comprising incorporating, in a photographic silver halide emulsion which contains a sensitizing dye, soft shellac, and then combining the emulsion with another photographic silver halide emulsion which differs in contrast from the first emulsion and which is devoid of sensitizing dyes.

10. A process for preparing a dye-sensitized mixed-grain photographic silver halide emulsion in which diffusion of the sensitizing dye is retarded comprising incorporating in a photographic silver halide emulsion which contains a sensitizing dye a substantially water-insoluble resin selected from the group consisting of whole shellac, hard shellac, soft shellac, hydrolyzed soft shellac, colophony, glyptal resins, gum mastic, dammar, sandarach, copal, kauri and coumarone resins, and then combining the emulsion with another photographic silver halide emulsion selected from the group consisting of those devoid of sensitizing dyes and those containing a sensitizing dye, the diffusion of which has been retarded by incorporating in the emulsion containing the sensitizing dye a substantially water-insoluble resin selected from the group consisting of whole shellac, hard shellac, soft shellac, hydrolyzed soft shellac, colophony, glyptal resins, gum mastic, dammar, sandarach, copal, kauri and coumarone resins.

11. A process for preparing a dye-sensitized mixed-grain variable contrast photographic silver halide emulsion in which diffusion of the sensitizing dye is retarded comprising incorporating in a photographic silver halide emulsion which contains a sensitizing dye from about 15 to about 35 grams for each gram-mole of silver halide in the emulsion, a substantially water-insoluble resin selected from the group consisting of whole shellac, hard shellac, soft shellac, hydrolyzed soft shellac, colophony, glyptal resins, gum mastic, dammar, sandarach, copal, kauri and coumarone resins, and then combining the emulsion which differs in contrast from the first emulsion and which is devoid of sensitizing dyes.

12. A mixed-grain photographic silver halide emulsion obtained according to the process defined by claim 1.

13. A mixed-grain variable contrast photographic silver halide emulsion obtained according to the process defined by claim 2.

14. A mixed-grain variable contrast photographic silver halide emulsion obtained according to the process defined by claim 3.

15. A mixed-grain photographic silver halide

emulsion obtained according to the process defined by claim 4.

16. A mixed-grain variable contrast photographic silver halide emulsion obtained according to the process defined by claim 5.

17. A mixed-grain photographic silver halide emulsion obtained according to the process defined by claim 6.

18. A mixed-grain variable contrast photographic silver halide emulsion obtained according to the process defined by claim 7.

19. A mixed-grain photographic silver halide emulsion obtained according to the process defined by claim 8.

20. A mixed-grain variable contrast photographic silver halide emulsion obtained according to the process defined by claim 9.

21. A mixed-grain variable contrast photographic silver halide emulsion obtained according to the process defined by claim 11.

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