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[54] PROCESS FOR SPECTRALLY SENSITIZING PHOTOGRAPHIC SILVER HALIDE EMULSIONS

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[51] **Int. Cl.** **G03c 1/08**, G03c 5/26

[58] **Field of Search** 96/102, 50, 85, 86, 87, 106

[56] **References Cited**

UNITED STATES PATENTS

3,469,987 9/1969 Owens et al. 96/102

OTHER PUBLICATIONS

Allingham et al., Adsorption of Dyes and Related Compounds by Silica, " Journal of Applied Chemistry," Vol. 8, February, 1958, pp. 108–116

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[57] **ABSTRACT**

A process for spectrally sensitizing photographic silver halide which comprises: adsorbing a photographic spectral sensitizing dye onto finely divided silica particles; and adding the dyed silica particles to a liquid photographic silver halide emulsion.

14 Claims, No Drawings

PROCESS FOR SPECTRALLY SENSITIZING PHOTOGRAPHIC SILVER HALIDE EMULSIONS

This invention relates to novel photographic processes, and more particularly to novel processes for spectrally sensitizing photographic silver halide emulsions. It also relates to novel photographic emulsions and elements prepared by the process of this invention.

The conventional method of sensitizing silver halide emulsions consists of dissolving the sensitizing dye in an appropriate organic solvent such as methyl alcohol, ethyl alcohol, acetone, etc., and adding the resulting solution to the liquid emulsion. While this general method has provided a commercially feasible means for incorporating sensitizing dyes into silver halide emulsions, it introduces undesirable amounts of organic solvent into the emulsion, which can result in coating defects or wandering of the dye in various layers of a photographic element.

It is therefore, an object of this invention to provide a new and improved method for incorporating sensitizing dyes into photographic silver halide emulsions.

Another object of this invention is to provide an efficient, readily controllable means for incorporating sensitizing dyes into such emulsions.

Another object is to provide novel silver halide emulsions and elements.

Other objects of this invention will be apparent from this disclosure and the appended claims.

I have made the important discovery that photographic spectral sensitizing dyes can be reversibly adsorbed to finely divided silica (SiO_2) particles. When the dyed silica particles are incorporated into a liquid photographic silver halide emulsion, the spectral sensitizing dye transfers to the silver halide crystals, and becomes effectively adsorbed thereto. This results in spectral sensitization of the silver halide grains in the emulsion. The silica remains in photographic layers produced with emulsions prepared in accordance with this invention. The residual silica in the layers inhibits dye wandering and provides tooth which facilitates retouching or writing thereon.

The method of this invention fully overcomes the mentioned shortcomings of the prior art procedures. The need of using organic solvents in the prior art processes to incorporate the dyes into the emulsions is completely eliminated in the method of this invention.

Suitable silicas for practicing this invention include silicon dioxide particles having an average diameter ranging from about 0.001 to 10 microns. Useful materials of this kind are commercially available under various trade names, e.g., Cab-o-Sil, a colloidal silica manufactured by Godfrey L. Cabot, Inc.; Celite, a diatomaceous silica manufactured by John-Manville Sales Corp.; Nalcosil, a colloidal silica manufactured by Nalco Chem. Co.; Hi-Sil, an ultra-fine silica manufactured by Pittsburgh Plate Glass Co.; Si-O-Lite, fine silica manufactured by Mallinkrodt Chem. Co.; powdered silica gels and the like. The concentration of the silica which is most advantageously employed will depend, of course upon the silver halide emulsion employed and upon the sensitizing dye employed. Ordinarily, however, from about 10 to 150 g., but preferably from about 15 to 50 g., of the silica per gram-mole of silver halide is advantageously used.

Suitable spectral sensitizing dyes for practicing the invention include any of those known to sensitize silver halide emulsions. Typical useful dyes include any of the methine dyes, such as the cyanine dyes (including the carbocyanines, the dicarbocyanines and complex cyanines); merocyanine dyes (including complex merocyanine dyes) and, styryl dyes. Typical dyes which can be used in the practice of this invention include any of those disclosed in the following patents, the disclosure of which is incorporated herein by reference.

Zeh et al. U.S. Pat. No. 2,068,047 issued 1/19/37
Brooker U.S. Pat. No. 2,078,233 issued 4/27/37
Koslowsky U.S. Pat. No. 2,107,279 issued 2/8/38
Mees U.S. Pat. No. 2,158,883 issued 5/16/39
Brooker et al. U.S. Pat. No. 2,161,331 issued 6/6/39
Brooker U.S. Pat. No. 2,170,807 issued 8/29/39

Brooker U.S. Pat. No. 2,177,402 issued 10/24/39
Brooker U.S. Pat. No. 2,177,403 issued 10/24/39
Carroll et al. U.S. Pat. No. 2,177,635 issued 10/31/39
Carroll U.S. Pat. No. 2,206,076 issued 7/2/40
Brooker U.S. Pat. No. 2,211,762 issued 8/20/40
Brooker et al. U.S. Pat. No. 2,213,238 issued 9/3/40
Brooker U.S. Pat. No. 2,307,916 issued 1/12/43
Brooker et al. U.S. Pat. No. 2,313,922 issued 3/16/43
Schneider U.S. Pat. No. 2,374,505 issued 4/24/45
Falleson et al. U.S. Pat. No. 2,378,917 issued 6/26/45
Brooker U.S. Pat. No. 2,454,629 issued 11/23/48
Thompson U.S. Pat. No. 2,535,993 issued 12/26/50
Carroll et al. U.S. Pat. No. 2,950,196 issued 8/23/60
Brooker et al. U.S. Pat. No. 2,955,939 issued 10/11/60
Jones U.S. Pat. No. 2,961,318 issued 11/22/60
Brooker et al. U.S. Pat. No. 3,194,805 issued 7/13/65
Tabor et al. U.S. Pat. No. 3,335,010 issued 8/8/67
Brooker et al. U.S. Reissue No. 24,292 reissued 3/19/57
I.G., British Pat. No. 434,235 accepted 8/28/35

The spectral sensitizing dye can be adsorbed to the silica in any convenient manner. Preferably, a spectral sensitizing dye is dissolved in an organic solvent for the dye, and the silica is mixed therewith. After the dye has become adsorbed to the silica, the organic solvent is advantageously removed in any convenient manner. Removal of the organic solvent is not essential to the practice of this invention; however, removal of the organic solvent is the preferred mode of carrying out the invention. Solvent removal can be accomplished in any convenient manner, e.g., by evaporation, filtration or centrifuging.

The concentration of the sensitizing dye can with advantage range from about 0.001 to 0.200 g. per gram-mole of silver halide in the emulsion. Advantageously, the dye-containing silica particles are incorporated in the photographic silver halide emulsions at temperatures ranging about from 40° to 60° C.

The process of this invention is useful in spectrally sensitizing any of the photographic silver halides, including silver bromide, silver chloride, silver bromoiodide, silver chlorobromide, silver chloroiodide or silver chlorobromoiodide. The photographic grains can be dispersed in any suitable binder, including such hydrophilic binders as gelatin, albumin, agaragar, gum arabic, alginic acid, polyvinyl alcohol, polyvinyl pyrrolidone, cellulose ethers, partially hydrolyzed cellulose acetate, and the like. The binding agents for the emulsion layer of the photographic element can also contain dispersed polymerized vinyl compounds. Such compounds are disclosed, for example, in U. S. Pat. Nos. 3,142,568; 3,193,386; 3,062,674 and 3,220,844 and include the water insoluble polymers of alkyl acrylates and methacrylates, acrylic acid, sulfoalkyl acrylates or methacrylates and the like.

Emulsions sensitized as described herein can be coated on any suitable photographic support, such as glass, film base such as cellulose acetate, cellulose acetate butyrate, polyesters such as poly(ethylene terephthalate), paper, baryta coated paper, polyolefin coated paper, e.g., polyethylene or polypropylene coated paper, which may be electron bombarded to promote emulsion adhesion, to produce the novel photographic elements of the invention.

Emulsions sensitized in accordance with this invention can contain addenda such as chemical sensitizers, e.g., sulfur sensitizers (e.g., allyl thiocarbamate, thiourea, allyl-isothiocyanate, cystine, etc.) various gold compounds (e.g., potassium chloroaurate, auric trichloride, etc. (see Baldsiefen, U.S. Pat. No. 2,540,085, issued Feb. 6, 1951, Damschroder, U.S. Pat. No. 2,597,856, issued May 27, 1952 and Yutzy et al. U.S. Pat. No. 2,597,915 issued May 27, 1952), various palladium compounds such as palladium chloride (Baldsiefen, U.S. Pat. No. 2,540,086, issued Feb. 6, 1951), potassium chloropalladate (Stauffer et al., U.S. Pat. No. 2,598,079, issued May 27, 1952), etc., or mixtures of such sensitizers; antifoggants such as ammonium chloroplatinate Trivelli et al. U.S. Pat. No. 2,566,245, issued Aug. 28, 1951), ammonium chloroplatinite (Trivelli et al., U.S. Pat. No. 2,566,263, issued Aug. 28, 1951), benzotriazole, nitrobenzimidazole, 5-nitroimidazole,

benzidine, mercaptans, etc. (see Mees–"The Theory of the Photographic Process," MacMillan Pub., 1942, page 460), or mixtures thereof. The silver halide emulsions of the invention can be hardened with any suitable hardener, including aldehyde hardeners such as formaldehyde, and mucochloric acid, aziridine hardeners, hardeners which are derivatives of dioxane, oxypolysaccharides such as oxy starch or oxy plant gums, and the like. The emulsion layers can also contain additional additives, particularly those known to be beneficial in photographic emulsions, including, for example, lubricating materials, stabilizers speed increasing materials, absorbing dyes, plasticizers, and the like. These photographic emulsions can also contain in some cases additional spectral sensitizing dyes. Furthermore, these emulsions can contain color-forming couplers or can be developed in solutions containing couplers or other color generating materials. Among the useful color formers are the monomeric and polymeric color formers, e.g., pyrazolone color formers, as well as phenolic, heterocyclic and open chain couplers having a reactive methylene group. The color-forming couplers can be incorporated into the photographic silver halide emulsion using any suitable technique, e.g., techniques of the type shown in Jelley et al. U.S. Pat. No. 2,322,027, issued June 15, 1943, Fierke et al. U.S. Pat. No. 2,801,171, issued July 30, 1957, Fisher U.S. Pat. Nos. 1,055,155 and 1,102,028, issued Mar. 4, 1913 and June 30, 1914, respectively, and Wilmanns U.S. Pat. No. 2,186,849, **issued Jan.** 9, 1949. They can also be developed using incorporated developers such as polyhydroxybenzenes, aminophenols, 3-pyrazolidones, and the like.

The following examples are included for a further understanding of this invention. Dyes used in the examples are identified in Table I.

TABLE I

Dye No.	Dye Compound
I	1,1'-Diethyl-2,2'-cyanine chloride
II	Anhydro-5,5',6,6'-tetrachloro-1,1'-diethyl-3,3'-di(3-sulfobutyl)benzimidazolocarbocyanine hydroxide
III	3-(3-Dimethylaminopropyl)-5-[(3-methyl-2-thiazolidinylidene)-ethylidene]-2-thio-2,4-oxazolidinedione

It will be understood that cyanine dye salts such as above Dye No. I include not only the chloride salt, but also the bromide, iodide, sulfamate, thiocyanate, perchlorate, p-toluenesulfonate, methyl sulfate, etc. salts.

The invention is further illustrated by the following examples of emulsions and elements prepared, and photographically tested, in accordance with this invention.

EXAMPLES 1 to 5

4 to 8 g. of each dye is dissolved in 20 ml. of an appropriate solvent such as methyl alcohol, and each solution is then added to 1.0 g. of finely divided silica (Cab-O-sil, a trade name for colloidal silica manufactured by Godfrey L Cabot, Inc.). Each mixture is centrifuged to separate the dyes silica from the solvent. The samples of dyed silica are in each case dried and powdered. The ratio of dye to silica will vary depending on the starting dye concentration, on the absorbing time, etc. These conditions can be adjusted in each case to produce a dye concentration giving the optimum sensitizing results. The dyed silica in each instance is then added directly to a stirred aqueous gelatin silver bromoiodide emulsion at 40° C. containing 0.77 mole percent iodide of the type described by Trivelli and Smith, Phot. Journal, 79, 330 (1939). The same batch of emulsion is used in each sample. The melts are held in each case at 52° C., cooled to 40° C., hand coated onto a cellulose acetate film support at a coverage of 432 mg. silver per square foot, chill set and dried. A sample of each coating is exposed to a wedge spectrograph, processed for 3 minutes in Kodak Developer D–19 which has the following composition:

N-methyl-p-aminophenol sulfate	2.0 g.
Hydroquinone	8.0 g.
Sodium sulfite (desiccated)	90.0 g.
Sodium carbonate (monohydrate)	52.5 g.
Potassium bromide	5.0 g.
Water to make	1.0 l.

and then fixed in a conventional sodium thiosulfate fixing bath, washed and dried. Densitometric measurements are then made of the developed images of each coating. The results are listed in the following Table 2 for sensitizing ranges and maximum sensitivities together with the respective concentrations of dye and silica corresponding to each of the examples.

TABLE 2

Example Number	Dye number	Approx. conc. of dye (g./mole silver)	Conc. of Cab-o-sil (g./mole silver)	Sensitization maximum, nm.	Sensitization range, nm.
	Control	None	24.8	440	to 515.
1	I	.092	24.8	575	to 600.
2	II	.0016	26.4	575	to 610.
3	II	.13	25.6	580	to 615.
4	III*	.12	26.8	515	to 560.
5	III*	.066	26.0	515	to 565.

*Coating contained 1.65 g. of Leucophor B/mole of silver (a stilbene type of brightening agent; colour index, 2nd edition, vol. 2, p. 2914).

Referring to the above table, it will be seen that in each of Examples 1 to 5 containing the indicated Dye Nos. I, II and III the sensitivity is extended to the region of 560 to 615 nm. with maximum sensitivity occuring in the region of 515 to 580 nm., whereas the control example containing approximately the same amount of silica but containing no sensitizing dye shows sensitivity up to about 515 nm. with a maximum sensitivity at 440 nm. Accordingly, these results clearly indicate that the novel process of this invention provides a new, effective and very convenient means for incorporating sensitizing dyes in photographic silver halide emulsions. These results further show that the resulting emulsions and elements faithfully extend the sensitivity in accordance with the sensitizing characteristics of each of the individual dyes.

It will be apparent from the foregoing disclosure that practically any spectral sensitizing cyanine dye can be substituted in the above examples to given generally similar good quality, spectrally sensitized silver halide emulsions and elements.

Although the invention has been described in considerable detail with particular reference to certain preferred embodiments thereof, it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove, and as defined in the appended claims.

I claim:

1. A process for spectrally sensitizing photographic silver halide which comprises: adsorbing a photographic spectral sensitizing dye onto finely divided silica particles; and, adding the dyed silica particles to a liquid photographic silver halide emulsion to transfer dye from the silica particles to the silver halide grains in said emulsion.

2. The process in accordance with claim **1** wherein said silica particles have an average diameter of from about 0.001 to 10 microns.

3. The process in accordance with claim **1** wherein said dye and said silica particles are present in proportions of about from 0.001 to 0.200 gram of said dye and about from 10 to 150 grams of said silica per gram-mole of silver halide in said emulsion.

4. the process in accordance with claim **3** wherein the photographic silver halide emulsion is an aqueous gelatin silver halide emulsion.

5. The process in accordance with claim **1** wherein said spectral sensitizing dye is selected from the group consisting of a cyanine dye and a merocyanine dye.

6. A process for spectrally sensitizing photographic silver halide which comprises: dissolving a photographic spectral

sensitizing dye in an organic solvent; mixing finely divided silica particles with a solution of dye in organic solvent to adsorb the dye onto the silica particles; removing the organic solvent; and, adding the dyed silica particles to a liquid photographic silver halide emulsion to transfer dye from the silica particles to the silver halide grains in said emulsion.

7. The process in accordance with claim 6, wherein said silica particles have an average diameter of from about 0.001 to 10 microns.

8. The process in accordance with claim 6 wherein said dye and said silica particles are present in the proportions of about from 0.001 to 0.200 gram of said dye and about from 10 to 150 grams of said silica per gram-mole of silver halide in said emulsion.

9. The process in accordance with claim 8 wherein the photographic silver halide emulsion in an aqueous gelatin silver halide emulsion.

10. The process in accordance with claim 3 wherein said silica particles comprise colloidal silica and said dye is a 1,1'-diethyl-2,2'-cyanine salt.

11. The process in accordance with claim 3 wherein said silica particles comprise colloidal silica and said dye is anhydro-5,5',6,6'1,1'-diethyl-3,3'-di(3-sulfobutyl)-benzimidazolocarbocyanine hydroxide.

12. The process in accordance with claim 3 wherein said silica particles comprise colloidal silica and said dye is 3-(3-dimethylaminopropyl)-5- -2-thio-2,4-oxazolidinedione.

13. A photographic silver halide emulsion prepared by the process of claim 1.

14. A photographic element comprising a support having thereon a layer containing a photographic silver halide emulsion prepared by the process of claim 1.

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