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ORGANIC THIOETHER OR SELENOETHER SILVER COMPLEXES AS EMULSION SENSITIZERS

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ABSTRACT OF THE DISCLOSURE

Photographic silver bromoiodide emulsions are spectrally sensitized by adding thereto a mixture comprising a photographic spectral sensitizing dye and a complex of silver with an organic thioether or an organic selenoether.

Addition of the silver complex reduces the blue desensitization caused by the sensitizing dye and thus increases spectral sensitization efficiency. Incubation stability of the emulsion is also enhanced.

This invention relates to photographic materials, and more particularly to a method for spectrally sensitizing photographic silver halide emulsions.

Williams and Cossar in U.S. Pat. 3,021,215, issued Feb. 13, 1962, in column 14, lines 27–33 describe the addition of poly(thiaalkylene diols) to spectrally sensitized gelatin silver bromoiodide emulsions. Such compounds increase the speed of photographic silver halide emulsions. Applicants' investigation of the use of various complexes in spectrally sensitizing silver halide emulsions indicates that an unrecognized phenomenon probably occurred when Williams and Cossar added poly(thiaalkylene diols) to spectrally sensitized silver bromoiodide emulsions. The poly(thiaalkylene diols) probably formed a complex with silver present in the silver halide crystals, and the silver-poly(thiaalkylene diol) complex possibly functioned to decrease the blue desensitization normally caused by photographic spectral sensitizing dyes. It would be desirable to provide still further decreases in the amount of desensitization caused by photographic spectral sensitizing dyes.

One object of this invention is to reduce the blue desensitization caused by photographic spectral sensitizing dyes.

Another object of this invention is to increase the efficiency of photographic spectral sensitization.

Still another object of this invention is to enhance the incubation stability of spectrally sensitized photographic silver halide emulsions.

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

In accordance with this invention, a photographic silver bromoiodide emulsion is spectrally sensitized by adding thereto a mixture comprising a photographic spectral sensitizing dye and a complex of silver with an organic thioether or an organic selenoether. Photographic emulsions spectrally sensitized in accordance with this invention exhibit reduced blue desensitization caused by the dye. The process of the invention increases the efficiency of spectral sensitization, both for molecular and J-band absorption. The invention also enhances the incubation stability of photographic emulsions, particularly those

emulsions sensitized with red and infrared photographic spectral sensitizing dyes.

In accordance with a preferred embodiment of this invention, the mixture of photographic spectral sensitizing dye and the silver complex are heated prior to incorporation in the silver bromoiodide emulsion. The heating step results in decreased dye desensitization, increased spectrally sensitized speeds and reduced fog.

In still another embodiment of this invention, photographic silver bromoiodide emulsions treated with a mixture comprising a photographic spectral sensitizing dye and a complex of silver with an organic thioether or selenoether are hypersensitized. Any of the conventional prior art hypersensitizing treatments can be utilized, including those mentioned by Mees and James, The Theory of the Photographic Process, 3rd Edition, published by the Macmillan Co., 1966, page 252, and including bathing the finished coating in water, an amine such as diethylamine, an ammoniacal solution or a solution of a silver salt, such as an aqueous solution of silver nitrite.

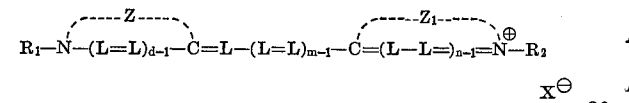
Coated emulsions are advantageously hypersensitized, e.g., by bathing in a dilute ammoniacal solution, such as 2 parts of 28% ammonia diluted with 100 parts water for 2 to 3 minutes at about 5° C. Other suitable means for hypersensitizing photographic emulsions appear in an article by Miller et al., Journal of the Photographic Society of America, vol. 12, pages 586–610, No. 10, November 1946.

The term "photographic spectral sensitizing dye" is used herein and in the appended claims as a word of art which denotes dyes employed as spectral sensitizers in negative, developing-out silver halide emulsions. Such dyes generally have a polarographic cathodic halfwave potential more positive than about −1.05 volts. In accordance with the present invention, cathodic measurements are made with a 1×10^{-4} molar solution of the dye in a solvent, for example, methanol which is 0.05 molar in lithium chloride using a dropping mercury electrode with the polarographic halfwave potential for the most positive cathodic wave being designated E_c. Anodic measurements are made with 1×10^{-4} molar aqueous solvent solution, for example, methanolic solutions of the dye which are 0.05 molar in sodium acetate and 0.05 molar in acetic acid using a carbon paste of pyrolytic graphite electrode, with the voltametric half peak potential for the most negative anodic response being designated E_a. In each measurement, the reference electrode is an aqueous silver-silver chloride (saturated potassium chloride) electrode at 20° C. Electrochemical measurements of this type are known in the art and are described in New Instrumental Methods in Electrochemistry, by Delahay, Interscience Publishers, New York, N.Y., 1954; Polarography, by Kolthoff and Lingane, 2nd Edition, Interscience Publishers, New York, N.Y., 1952; Analytical Chemistry, 36, 2426 (1964) by Elving; and Analytical Chemistry, 30, 1576 (1958) by Adams. The less negative (more positive) the cathodic (reduction) potential, the greater is the electron affinity of a dye and conversely the less positive (more negative) the anodic (oxidation) potential of a dye, the greater is its electron-donating ability.

The useful photographic spectral sensitizing dyes include the methine dyes, such as the cyanine, merocyanine, hemicyanine, oxonol and styryl dyes. Typical useful methine dyes are described in Brooker U.S. Pats. 1,846,-301, issued Feb. 23, 1932; 1,846,302, issued Feb. 23,

1932; and 1,942,854, issued Jan. 9, 1934; White U.S. Pat. 1,990,507, issued Feb. 12, 1935; Brooker and White U.S. Patents 2,112,140, issued Mar. 22, 1938; 2,165,338, issued July 11, 1939; 2,493,747, issued Jan. 10, 1950, and 2,739,964, issued Mar. 27, 1956; Brooker and Keyes U.S. Pat. 2,493,748, issued Jan. 10, 1950; Sprague U.S. Pats. 2,503,776, issued Apr. 11, 1950, and 2,519,001, issued Aug. 15, 1950; Heseltine and Brooker U.S. Pat. 2,666,761, issued Jan. 19, 1954; Heseltine U.S. Pat. 2,734,900, issued Feb. 14, 1956; Van Lare U.S. Pat. 2,739,149, issued Mar. 20, 1956; and Kodak Limited British Pat. 450,958, accepted July 15, 1936.

Preferred cyanine dyes which can be employed in accordance with this invention have the following general formula:

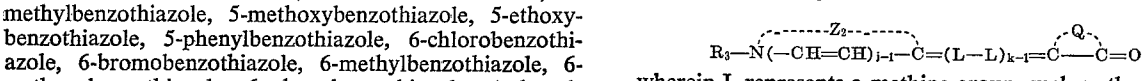


wherein *d* and *n* each represents a positive integer of from 1 to 2, *m* represents a positive integer of from 1 to 5, each L represents a methine group (e.g., —CH=, —C(CH$_3$)=, etc.), and Z and Z$_1$ each represents the non-metallic atoms necessary to complete a heterocyclic nucleus containing from 5 to 6 atoms in the heterocyclic ring, e.g., thiazole, 4-phenylthiazole, 4,5-diphenylthiazole, 4-(2-thienyl)thiazole, 4-methylthiazole, benzothiazole, 4-chlorobenzothiazole, 4-methylbenzothiazole, 4-methoxybenzothiazole, 4-ethoxybenzothiazole, 4-phenylbenzothiazole, 5-chlorobenzothiazole, 5-bromobenzothiazole, 5-methylbenzothiazole, 5-methoxybenzothiazole, 5-ethoxybenzothiazole, 5-phenylbenzothiazole, 6-chlorobenzothiazole, 6-bromobenzothiazole, 6-methylbenzothiazole, 6-methoxybenzothiazole, 6-ethoxybenzothiazole, 4-phenyloxazole, benzoxazole, 5-chlorobenzoxazole, 5-methylbenzoxazole, 5-bromobenzoxazole, 5-methoxybenzoxazole, 5-ethoxybenzoxazole, 5-phenylbenzoxazole, 1,3-dialkyl, 1,3-diaryl or 1-alkyl-3-aryl, imidazoles and benzimidazoles, such as 5-chloro-1,3-dialkyl benzimidazoles, 5-chloro-1,3-diaryl benzimidazoles, 5,6-dichloro-1,3-dialkyl benzimidazoles, 5,6-dichloro-1,3-diaryl benzimidazoles, 5-methoxy-1,3-dialkyl benzimidazoles, 5-methoxy-1,3-diaryl benzimidazoles, 5-cyano-1,3-dialkyl benzimidazoles, 5-cyano-1,3-diaryl benzimidazoles, 1,3-dialkylnaphth[1,2-d]imidazole, 1,3-diarylnaphth[2,1-d]imidazole, 4-methylselenazole, 4-phenylselenazole, selenazole, benzoselenazole, 5-chlorobenzoselenazole, α-naphthothiazole, β-naphthothiazole, quinoline, 6-methylquinoline, 6-methoxyquinoline, 6-ethoxyquinoline, 6-chloroquinoline, 4-methoxyquinoline, 4-ethoxyquinoline, 4-methylquinoline, 8-methoxyquinoline, β-methylquinoline, 4-chloroquinoline, 3,3-dimethylindolenine, etc.; X represents an acid anion, such as chloride, bromide, p-toluene sulfonate, methane sulfonate, methylsulfate, ethylsulfate, perchlorate, etc.; R$_1$ and R$_2$ each represents an alkyl group (including substituted alkyl) having from 1 to 18, and preferably 1 to 4 carbon atoms, such as methyl, ethyl, propyl, isopropyl, butyl, sec-butyl, hexyl, dodecyl, octadecyl, benzyl, β-phenylethyl sulfoalkyl such as β-sulfoethyl, γ-sulfopropyl, γ-sulfobutyl, δ-sulfobutyl, etc.; carboxyalkyl such as β-carboxyethyl, γ-carboxypropyl, δ-carboxybutyl, etc.; sulfatoalkyl such as γ-sulfatopropyl and δ-sulfatobutyl, etc., or an alkylene chain which joins with a methine linkage, such as a butylene or neopentylene linkage, or an aryl group such as phenyl, naphthyl, tolyl, p-chlorophenyl, etc. It will be noted that in some instances, the acid anion, represented by X in the above formula, is included in the substituent represented by R$_2$, such as dyes containing the betaine type structure. Some specific useful cyanine dyes are listed below:

1',3-diethylthia-2'-cyanine chloride
1,1'-diethyl-2,2'-cyanine chloride
3,3'-diethyloxacarbocyanine iodide
5,5'-dichloro-3,3'-diethylthiacarbocyanine iodide

1,1'-diethyl-2,2'-carbocyanine iodide
3,3'-diethylthiazolocarbocyanine iodide
3,3'-diethyl-4,4'-dephenylthiazolocarbocyanine iodide
3,3'-diethyl-9-methylthiacarbocyanine iodide
1,3,3'-triethylbenzimidazole-oxacarbocyanine iodide
5-chloro-1,3,3'-triethylbenzimidazolo-oxacarbocyanine iodide
5,6-dichloro-1,3,3'-triethylbenzimidazolothiacarbocyanine iodide
1,1'-3-triethylbenzimidazolo-2'-carbocyanine iodide
1,1',3-triethylbenzimidazolo-4'-carbocyanine iodide
1,1'-diethyl-2,4'-carbocyanine iodide
1',3-diethyl-4-methylthiazolo-2'-carbocyanine iodide
3,3'-diethylthiadicarbocyanine iodide
1,1'-diethyl-2,2'-dicarbocyanine iodide
1',3-diethylthia-2'-dicarbocyanine iodide
Anhydro-5,5'-6,6-tetrachloro-1,1',3-triethyl-3'-(4-sulfobutyl)-benzimidazolocarbocyanine hydroxide
Anhydro-5,6-dichloro-1-ethyl-3-(3-sulfobutyl)-3'-(3-sulfopropyl)-4',5'-benzobenzimidazolothiacarbocyanine hydroxide
1,1',3,3'-tetraethyl-naphth[1,2-d]imidazolocarbocyanine iodide
Anhydro-5,6-dichloro-1,3-diethyl-(3'-sulfobutyl)-benzimidazoloselenacarbocyanine hydroxide
1,2-diethylthia-4'-carbocyanine iodide
Anhydro-5,5',6,6'-tetrachloro-1,1'-diethyl-3,3'-di(4-sulfobutyl)-benzimidazolocarbocyanine hydroxide

Merocyanine dyes especially useful in this invention have the following formula:



wherein L represents a methine group, such as those mentioned above; Z$_2$ is selected from a value given for Z and Z$_1$, above; R$_3$ is an alkyl or aryl group, such as those referred to above; *j* and *k* each represents a positive integer of from 1 to 2; and Q represents the non-metallic atoms necessary to complete a heterocyclic ketomethylene nucleus of the type used in merocyanine dyes typically containing hetero atoms selected from nitrogen, sulfur, selenium and oxygen, such as a 1,3-dioxane-4,6-dione nucleus, e.g., 2,2-dialkyl-1,3-dioxane-4,6-dione, etc.; a 2-pyrazolin-5-one nucleus; e.g., 3-methyl-1-phenyl-2-pyrazolin-5-one, 1-phenyl-2-pyrazolin-5-one, 1-(2-benzothiazolyl)-3-methyl-2-pyrazolin-5-one, etc.; an isoxazolone nucleus, e.g., 3-phenyl-5-(4H)-isoxazolone, 3-methyl-5(4H)-isoxazolone, etc.; an oxindole nucleus, e.g., 1-alkyl-2-oxindoles, etc.; a 2,4,6-triketohexahydropyrimidine nucleus, e.g., barbituric acid or 2-thiobarbituric acid as well as their 1-alkyl (e.g., 1-methyl, 1-ethyl, 1-propyl, 1-heptyl, etc.) or 1,3-dialkyl (e.g., 1,3-dimethyl, 1,3-diethyl, 1,3-dipropyl, 1,3-diisopropyl, 1,3-dicyclohexyl, 1,3-di(β-methoxyethyl), etc.; or 1,3-diaryl (e.g., 1,3-diphenyl, 1,3-di(p-chlorophenyl), 1,3-di(p-ethoxycarbonylphenyl), etc.); or 1-aryl (e.g., 1-phenyl, 1-p-chlorophenyl, 1-p-ethoxycarbonylphenyl), etc.) or 1-alkyl-3-aryl (e.g., 1-ethyl-3-phenyl, 1-n-heptyl-3-phenyl, etc.) derivatives, a rhodanine nucleus (i.e., 2-thio-2,4-thiazolidinedione series), such as rhodanine, 3-alkylrhodanines, e.g., 3-ethylrhodanine, 3-allylrhodanine, etc., 3-carboxyalkylrhodanines, e.g., 3-(2-carboxyethyl)rhodanine, 3-(4-carboxybutyl)rhodanine, etc., 3-sulfoalkylrhodanines, e.g., 3-(2-sulfoethyl)rhodanine, 3-(3-sulfopropyl)rhodanine, 3-(4-sulfobutyl)rhodanine, etc., or 3-arylrhodanines, e.g., 3-phenylrhodanine, etc., a 2-(3H)-imidazo[1,2-a]pyridone nucleus; a 5,7-dioxo-6,7-dihydro-5-thiazolo[3,2-a]pyrimidine nucleus, e.g., 5,7-dioxo-3-phenyl-6,7-dihydro-5-thiazolo[3,2-a]pyrimidine, etc.; a 2-thio-2,4-oxazolidinedione nucleus (i.e., those of the 2-thio-2,4(3H,5H)-oxazoledione series) e.g., 3-ethyl-2-thio-2,4-oxazolidinedione, 3-(2-sulfoethyl)-2-thio-2,4-oxazolidinedione, 3-(4-sulfobutyl)-2-thio-2,4-oxazolidinedione, 3-(3-carboxypropyl)-2-thio-2,4-oxazolidinedione, etc.; a thianaphthenone nucleus, e.g., 3-(2H)-thianaphthenone, etc.; a 2-thio-2,5-

thiazolidinedione nucleus (i.e., the 2-thio-2,5-(3H,4H)-thiazoledione series), e.g., 3-ethyl-2-thio-2,5-thiazolidinedione, etc.; a 2,4-thiazolidinedione nucleus, e.g., 2,4-thiazolidinedione, 3-ethyl-2,4-thiazolidinedione, 3-phenyl-2,4 - thiazolidinedione, 3-α-naphthyl-2,4-thiazolidinedione, etc.; a thiazolidinone nucleus, e.g., 4-thiazolidinone, 3-ethyl-4-thiazolidinone, 3-phenyl-4-thiazolidinone, 3-α-naphthyl-4-thiazolidinone, etc.; a 2-thiazolin-4-one nucleus, e.g., 2-ethylmercapto-2-thiazolin-4-one, 2-alkylphenylamino-2-thiazolin - 4 - one, 2-diphenylamino-2-thiazolin-4-one, etc.; a 2-imino-4-oxazolidinone (i.e., pseudohydantoin) nucleus; a 2,4-imidazolidinedione (hydantoin) nucleus, e.g., 2,4-imidazolidinedione, 3-ethyl-2,4-imidazolidinedione, 3-phenyl-2,4-imidazolidinedione, 3-α-naphthyl-2,4-imidazolidinedione, 1,3-diethyl-2,4-imidazolidinedione, 1-ethyl - 3 - phenyl - 2,4 - imidazolidinedione, 1-ethyl-3-α-naphthyl-2,4-imidazolidinedione, 1,3-diphenyl - 2,4 - imidazolidinedione, etc.; a 2-thio-2,4-imidazolidinedione (i.e., 2-thiohydantoin) nucleus, e.g., 2-thio-2,4-imidazolidinedione, 3-ethyl-2-thio-2,4-imidazolidinedione, 3-(4-sulfobutyl)-2-thio-2,4-imidazolidinedione, 3-(2-carboxyethyl)-2-thio-2,4-imidazolidinedione, 3-phenyl - 2 - thio-2,4-imidazolidinedione, 3 - α - naphthyl - 2 - thio-2,4-imidazolidine dione, 1,3-diethyl-2-thio-2,4-imidazolidinedione, 1-ethyl-3-phenyl-2-thio-2,4-imidazolidinedione, 1 - ethyl-3-α-naphthyl-2-thio - 2,4 - imidazolidinedione, 1,3-diphenyl-2-thio-2,4-imidazolidinedione, etc.; a 2-imidazolin-5-one nucleus, e.g., 2-propylmercapto-2-imidazolin-5-one, etc. Preferably, Q_1 and Q_2 each represents the atoms to complete a ring containing from 3 to 4 carbon atoms, one nitrogen atom and one atom selected from the group consisting of nitrogen, oxygen, sulfur and selenium. Typical useful merocyanine dyes are described, for example, in Brooker et al. U.S. Pats. 2,493,747 and 2,493,748, both issued Jan. 10, 1950.

Particularly good results are obtained with the following cyanine and merocyanine dyes:

3,3'-diethyl-9,11,15,17-dineopentylenethiapentacarbocyanine iodide
3,3'-diethylselenadicarbocyanine iodide
1,3-diethyl-5-[4-(3-ethyl-2-benzothiazolinylidene)-2-butenylidene]-2-thiobarbituric acid
3,3'-diethylthiacarbocyanine chloride
3,3'-diethylcyanine chloride
3,3'-diethylcarbocyanine iodide
5,5',6,6'-tetrachloro-1,1',3,3'-tetraethylbenzimidazolocarbocyanine chloride
Anhydro-5,5',6,6'-tetrachloro-1,1'-diethyl-3,3'-di(3-sulfobutyl)benzimidazolocarbocyanine hydroxide
Anhydro-5,5',6,6'-tetrachloro-1,1',3-triethyl-3'-(3-sulfobutyl)benzimidazolocarbocyanine hydroxide
5,5'-dichloro-3,3'-diethyl-9-phenylselenacarbocyanine iodide
3,3',9-triethyl-5,6,5',6'-dibenzothiacarbocyanine p-toluenesulfonate

If desired, combinations of photographic spectral sensitizing dyes can be employed in the practice of the invention.

Any silver complex with an organic thioether compound or an organic selenoether compound can be utilized in the practice of this invention. A preferred class of complexes are those of silver with an alkane or cycloalkane containing from 5 to 30 carbon atoms in which from 2 to 6 —CH_2— groups, but not more than one half of the total number of —CH_2— groups, are replaced with a divalent selenium or, preferably, a divalent sulfur atom. Dithia-tetraoxacyclooctadecanes are especially useful silver complexing agents. Some organic thioether and selenoether compounds which form particularly useful silver complexes are set out below:

1,4-bis(5-hydroxy-3-thiapentyl)piperazine
3,4-diaza-1,16-dithia-9,12,15-trioxa-2,4-cycloheptadecadiene-2,5-sulfide.
Poly[2,2'-thiodiethylsuccinate]
1,10-dithia-4,7,13,16-tetraoxacyclooctadecane
4,7,13,16-tetraoxa-1,10-diselenocyclooctadecane
Poly[thiodiethylene glutarate]
1,3-bis(4-phenyl-1,2,4-triazol-3-ylthio)propane
1,8-dihydroxy-3,6-dithiaoctane
Bis(3-oxapentamethylene carbamyloxyethyldisulfide)

The complex of silver with the organic thioether or selenoether can be prepared in any convenient manner prior to incorporation in the emulsion. Advantageously, the complexing agent is mixed with a suitable source, such as silver nitrate in a common solvent. The mixture of sensitizing dye and silver complexing agent can be formulated in any convenient manner. For example, a silver source, such as silver nitrate, can be added to a solution containing the organic thioether or selenoether complexing agent and dye. The solvent is not critical; any solvent is useful which dissolves the dye, silver source, complexing agent and the silver complex formed. Methanol is a solvent for many photographic sensitizing dyes and provides good results. Other typical useful solvents include ethanol, isopropanol, pyridine, etc.

Preferably the mixture of dye and silver-organic thioether or selenoether complex is heated just prior to incorporation in the emulsion. Heating a solution of dye and silver-organic complex to temperatures of about 30 to 80° C., and preferably about 40 to 60° C., and maintaining the solution at that temperature from about 2 minutes to one hour, and preferably about 5 to 10 minutes, provides excellent increases in the spectrally sensitized speed of emulsions sensitized.

The photographic spectral sensitizing dye is incorporated in the emulsions in concentrations sufficient to spectrally sensitize the emulsion. Typical dyes function as efficient spectral sensitizers in concentrations of from about .001 to about .300 gram per mole of silver in the emulsion.

The silver-organic complex is incorporated in the emulsions in concentrations sufficient to decrease the blue desensitization caused by the photographic sensitizing dye, and to increase the efficiency of spectral sensitization by the dye. Amounts of about 0.25 to about 0.75 gram of silver complex per mole of silver halide in the emulsions provide satisfactory results.

The process of the invention is useful in spectrally sensitizing photographic silver bromoiodide emulsions. The halide of such emulsions preferably contains at least 60%, and preferably at least 80 to 90% bromide. Other photographic silver halides, such as silver chlorobromide, are ripened (i.e., the grains grow larger) by the complexing agents employed herein.

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, allylisothiocyanate, cystine, etc.) various gold compounds (e.g., potassium chloroaurate, auric trichloride, etc. (see Baldsiefen U.S. Pat. 2,540,085, issued Feb. 6, 1951; Damschroder U.S. Pat. 2,597,856, issued May 27, 1952 and Yutzy et al. U.S. Pat. 2,597,915, issued May 27, 1952), various palladium compounds such as palladium chloride (Baldsiefen U.S. Patent 2,540,086, issued Feb. 6, 1951), potassium chloropalladate (Stauffer et al. U.S. Patent 2,598,079, issued May 27, 1952), etc., or mixtures of such sensitizers; antifoggants such as ammonium chloroplatinate (Trivelli et al. U.S. Patent 2,566,245, issued Aug. 28, 1951), ammonium chloroplatinate (Trivelli et al. U.S. Patent 2,566,263, issued Aug.

28, 1951), benzotriazole, nitrobenzimidazole, 5-nitroimidazole, benzidine, mercaptans, etc. (see Mees and James, The Theory of the Photographic Process, Macmillan Publishers, 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 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. 2,322,027, issued June 15, 1943, Fierke et al. U.S. Pat. 2,801,171, issued July 30, 1957, Fisher U.S. Pats. 1,055,155 and 1,102,028, issued Mar. 4, 1913 and June 30, 1914, respectively, and Wilmanns U.S. Pat. 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.

EXAMPLE 1

A sulfur and gold sensitized, large grain, liquid gelatin silver bromoiodide (about 6 mole percent of the halide being iodide) emulsion is stirred thoroughly, combined with a suitable surfactant (e.g., saponin) and hardener (e.g., formaldehyde) and coated on a cellulose acetate support at a coverage of 350 mg. silver and 810 mg. gelatin per square foot. One set of coatings is exposed to tungsten light on an Eastman 1B sensitometer and processed for 5 minutes at 20° C. in Kodak D–50 developer. The relative speed values obtained are given in Table I. The relative blue speed is obtained by exposing the element through a combination of filters: Wratten 35 plus 38A plus a blue filter that absorbs green and red light and transmits blue light.

EXAMPLE 2

The procedure of Example 1 is followed except that infrared sensitizing dyes I and II (identified at the end of Table I) are added to the emulsion along with the silver complexing agent 1,10-dithio - 4,7,13,16 - tetraoxacyclooctadecane (which forms a silver complex with silver ion in the emulsion). The infrared speed is determined by exposure on the sensitometer through a Wratten 89B filter. The results appear in Table I.

EXAMPLES 3–5

The procedure of Example 2 is repeated except that the complexing agent and sensitizing dyes I and II are dissolved in methanol with varying amounts of silver nitrate and the mixture obtained is added to the emulsion. The results appear in Table I.

EXAMPLES 6–8

The procedure of Examples 3–5 is repeated except that the methanolic solution of sensitizing dyes, silver complexing agent and silver nitrate is heated to 50° C., held at that temperature for 6 minutes, and then added to the emulsion. The results are shown in Table I.

TABLE I

Example	Sensitizing dyes	Complexing agent	Mg. $AgNO_3$ mole Ag	Relative blue speed	Relative infrared speed	$D_{min.}$
1				331		.06
2	I, II	D		100	100	.06
3	I, II	D	[1] 120	115	110	.06
4	I, II	D	[1] 240	138	145	.06
5	I, II	D	[1] 480	151	182	.10
6	I, II	D	[2] 120	115	120	.04
7	I, II	D	[2] 240	115	138	.06
8	I, II	D	[2] 480	159	209	.06

[1] All chemicals pre-mixed in methyl alcohol, then added to the emulsion.
[2] All chemicals pre-mixed in methyl alcohol, heated to 50° C., held 6 min., and then added to the emulsion.

NOTE.—Dye I: 3,3'-diethylselenodicarbocyanine iodide. Dye II: Anhydro-1-ethyl-3-(3-sulfobutyl)thia-2'-cyanine hydroxide. D: 1,10-dithia-4,7,13,16-tetraoxacyclooctadecane.

Exposure: 1/5 second 500 w. 5400° K.
Processing: 5 minutes Kodak D–50 developer

The data in Table I shows that the ex situ preparation of the silver complex-dye mixture is more efficient than the in situ formation of the silver complex of the organic ligand, D (Example 2 versus Examples 3–8). Examples 3–5 and 6–8 indicate that the amount of silver nitrate available to form the silver complex has a marked influence on the efficiency of the supersensitization. In addition, a heat treatment during the pre-mixing step causes a further gain in spectrally sensitized speed. It is believed that the ex situ mixing of silver nitrate, organic ligand and sensitizing dye alone or with a heat treatment, facilitates the formation of the silver complex which in turn acts as a more efficient supersensitizer for the sensitizing dye combination (Dye I and Dye II). Note that the heat treatment step prevents the undue formation of fog (Example 5 versus 8). The ex situ preparation of the silver-organic complex, and the pre-mixing of the sensitizing dye and the silver-organic complex, produces increased blue (intrinsic) sensitivity, higher spectral sensitivity and reduced minimum densities. Results generally similar to those in Table I are obtained when other spectral sensitizing dyes, such as those mentioned above, and when other organic thioether or selenoether complexing agents, are used in place of Dyes I and II and Complexing Agent D. Dyes which spectrally sensitize to shorter wavelengths than infrared are useful in the invention, and are supersensitized in the general region in which they spectrally sensitize.

EXAMPLE 9

A non-spectrally sensitized control coating is prepared and coated as in Example 1. The dried element is exposed and processed as in Examples 1–8, except that a Wratten 29 filter (red) is substituted for the Wratten 89B filter. An additional set of coatings is hypersensitized by bathing for 2 to 3 minutes in a 5° C. solution consisting of 2 parts 28% aqueous ammoniacal solution and 100 parts water, rinsed in methanol, dried, immediately exposed and processed as the control coating. The unhypered coating is assigned a blue speed of 100 and has a minimum density of 0.04. The ammonia hypered coating has a relative blue speed of 138 and a minimum density of 0.06.

EXAMPLES 10–23

The procedure set out in Example 9 is followed with the exception that the emulsion is spectrally sensitized with a pre-mixed, pre-heated solution consisting of a spectral sensitizing dye (at various levels), and 0.6 gram of silver complex per silver mole of emulsion. The silver complexing agent (D) is identical to the one used in Examples 2–8. The sensitometric data obtained from these unhypered and hypered coatings are listed in Table II. The following individual sensitizing dyes are incorporated in the coatings:

(III) 5,5'-dichloro-3,3'-diethyl-9-phenylselenacarbocyanine iodide

(IV) 3,3'-9-triethyl-5,6,5',6'-dibenzothiacarbocyanine p-toluenesulfonate

(V) 5,5'-dichloro-3,3',9-triethylthiacarbocyanine bromide

(VI) 3,3'-dimethyl-9-phenylthiacarbocyanine iodide

TABLE II

Example	Format: Dye at mg./mole silver ± complex at 0.6 g./mole silver	Unhypered: Relative blue speed	Unhypered: Relative red speed	Unhypered: $D_{min.}$	Ammonia hypered: Relative blue speed	Ammonia hypered: Relative red speed	Ammonia hypered: $D_{min.}$
9	None	100	----------	.04	138	----------	.06
10	150 mg. dye III	83	105	.06	120	417	.08
11	300 mg. dye III	53	110	.08	91	525	.10
12	150 mg. dye III plus complex	120	398	.06	120	692	.08
13	300 mg. dye III plus complex	110	525	.08	115	795	.10
14	100 mg. dye IV	95	159	.06	105	302	.10
15	200 mg. dye IV	87	219	.10	91	380	.14
16	100 mg. dye IV plus complex	105	219	.08	95	251	.10
17	200 mg. dye IV plus complex	110	380	.12	83	363	.14
18	150 mg. dye V	100	219	.06	105	417	.08
19	300 mg. dye V	80	251	.10	73	398	.12
20	150 mg. dye V plus complex	115	316	.06	95	363	.08
21	300 mg. dye V plus complex	100	380	.14	80	417	.14
22	250 mg. dye VI	42	21	.10	46	83	.10
23	250 mg. dye VI plus complex	76	55	.10	73	132	.12

A study of the data in Table II reveals that unhypered coatings, containing both the dye and the silver complex, show equal or nearly equal red speeds in comparison with the hypered coatings containing an equal amount of sensitizing dye and no silver complex. For instance, compare Example 13 (unhypered) with Example 11 (hypered), Example 17 (unhypered) with Example 15 (hypered), Example 21 (unhypered) with Example 19 (hypered) and Example 23 (unhypered) with Example 22 (hypered). In most cases the unhypered coatings have less fog. In some examples the hypered coatings containing a silver complexing agent have more speed than hypered coatings containing a sensitizing dye and no complexing agent. For example, compare the hypered coatings of Examples 10 and 11 (no complex) with Examples 12 and 13 (complex).

EXAMPLES 24–32

Mees and James in The Theory of the Photographic Process, 3rd Edition, published by the Macmillan Co., New York, 1966, state at page 258, that dye desensitization increases with increasing pAg. However, lowering the pAg of a coating causes a loss in storage stability and an increase in fog. These examples demonstrate that the use of a silver complexing agent with a spectral sensitizing dye duplicates the sensitometric advanges of low pAg coatings with the dye alone, without an increase in fogging propensity upon incubation. The emulsion, coating format, exposure and processing procedures are the same as in Examples 9–23. The final pAg of the final emulsion composition is adjusted with a solution of silver nitrate. Table III contains the sensitometric data obtained from these examples. The complexing agent is 1,10-dithia-4,7,13,16-tetraoxacyclooctadecane (D).

TABLE III

Example	160 mg. dye/mole Ag ± complex at 0.6 g./mole Ag	pAg	Relative blue speed	Relative red speed	Fog	1 wk. 120° F. 50% R.H. incubation fog
24	None (control)	8.2	100	----------	.06	.04
25	Dye III	8.2	40	87	.06	.06
26	Dye III plus complex	8.2	67	263	.06	.06
27	None (control)	7.8	110	----------	.04	.05
28	Dye III	7.8	58	132	.08	.06
29	Dye III plus complex	7.8	73	302	.07	.07
30	None (control)	7.4	63	----------	.36	.52
31	Dye III	7.4	95	276	.16	.15
32	Dye III plus complex	7.4	69	316	.14	.20

NOTE.—Dye III: 5,5'-dichloro-3,3'-diethyl-9-phenylselenacarbocyanine iodide. Complexing Agent D: 1,10-dithia-4,7,13,16-tetraoxacyclooctadecane. Exposure: 1/5 second 500W 5,400° K. Processing: 5 minutes Kodak D-50 developer.

The sensitometric results in Table III show that by using a silver complex in conjunction with a sensitizing dye at a normal pAg of 8.2, one can almost duplicate the red speed obtained by lowering the pAg (7.4) of a spectrally sensitized coating containing no silver complex without encountering the increased fogging tendency at the lower pAg. Compare Example 26 with Example 31.

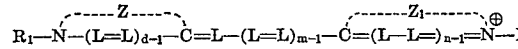
The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention described hereinabove and in the appended claims.

We claim:

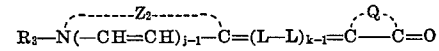
1. The method of spectrally sensitizing a photographic silver bromoiodide emulsion which comprises adding to said emulsion a mixture comprising a photographic spectral sensitizing dye and a complex of silver with an organic thioether or an organic selenoether.

2. The method of spectrally sensitizing a photographic silver bromoiodide emulsion which comprises adding to said emulsion a mixture comprising:

(a) a photographic spectral sensitizing dye having one of the following formulas:



and



wherein Z, Z_1 and Z_2 each represents the non-metallic atoms required to complete a heterocyclic nucleus containing from 5 to 6 atoms in the heterocyclic ring; each L represents a methine linkage; R_1, R_2 and R_3 each represents an alkyl group, an alkylene group joined to a methine linkage, or an aryl group; Q represents the non-metallic atoms required to complete a heterocyclic ketomethylene nucleus containing from 5 to 6 atoms in the heterocyclic ring; *m* represents an integer of from 1 to 5; *d*, *n* and *j* each represents an integer of from 1 to 2; *k* represents an integer of from 1 to 3; and X represents an acid anion; and

(b) a complex of silver with an alkane or cycloalkane containing from 5 to 20 carbon atoms in which from 2 to 6 —CH_2— groups, but not more than one half the total number of —CH_2— groups, are replaced with a divalent sulfur or selenium atom.

3. The process of claim 2 wherein said complex of silver is a silver-dithia-tetraoxacyclooctadecane complex.

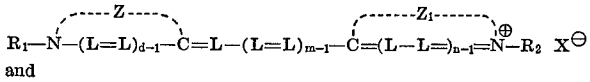
4. The metod of spectrally sensitizing a photographic silver bromoiodide emulsion which comprises adding to

said emulsion a methanolic solution comprising the photographic spectral sensitizing dyes 3,3'-diethylselenodicarbocyanine salt and anhydro-1-ethyl-3-(3-sulfobutyl)thia-2'-cyanine salt, and a complex of silver with 1,10-dithia-4,7,13,16-tetraoxacyclooctadecane.

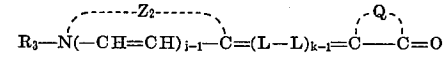
5. The method of spectrally sensitizing a photographic silver bromoiodide emulsion which comprises heating a solution of a silver salt, an organic thioether or an organic selenoether, and a photographic spectral sensitizing dye; and, adding said heated solution to said silver bromoiodide emulsion.

6. The method of spectrally sensitizing a photographic silver bromoiodide emulsion which comprises heating for about 2 minutes to one hour, at about 30 to 80° C., a solution comprising:

(a) a photographic spectral sensitizing dye having one of the following formulas:



and



wherein Z, Z_1 and Z_2 each represents the non-metallic atoms required to complete a heterocyclic nucleus containing from 5 to 6 atoms in the heterocyclic ring; each L represents a methine linkage; R_1, R_2 and R_3 each represents an alkyl group, an alkylene group joined to a methine linkage, or an aryl group; Q represents the non-metallic atoms required to complete a heterocyclic ketomethylene nucleus containing from 5 to 6 atoms in the heterocyclic ring; *m* represents an integer of from 1 to 5; *d n* and *j* each represents an integer of from 1 to 2; *k* represents an integer of from 1 to 3; and, X represents an acid anion;

(b) a complex of silver with an alkane or cycloalkane containing from 5 to 20 carbon atoms in which from 2 to 6 —CH_2— groups, but not more than one half the total number of —CH_2— groups, are replaced with a divalent sulfur or selenium atom; and adding said heated solution to said emulsion.

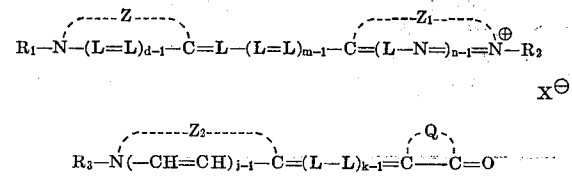
7. The method of claim **6** wherein said heat treatment is conducted for about 5 to 10 minutes at a temperature of between 40° and 60° C.

8. The method of spectrally sensitizing a photographic silver bromoiodide emulsion which comprises heating for 5 to 10 minutes, at 40 to 60° C. a methanolic solution containing the sensitizing dyes 3,3'-diethylselenodicarbocyanine salt and anhydro-1-ethyl-3-(3-sulfobutyl)thia-2'-cyanine salt and, a complex of silver with 1,10-dithia-4,7, 13,16-tetraoxacyclooctadecane; and, adding said heated solution to said emulsion.

9. The process of sensitizing a photographic silver bromoiodide emulsion which comprises adding to said emulsion a mixture comprising a photographic spectral sensitizing dye and a complex of silver with an organic thioether or selenoether; coating said emulsion on a support; and, bathing said coated emulsion in a hypersensitizing bath.

10. The process of sensitizing a photographic silver bromoiodide emulsion which comprises adding to said emulsion a mixture comprising:

(a) a photographic spectral sensitizing dye having one of the following formulas;



wherein Z, Z_1 and Z_2 each represents the non-metallic atoms required to complete a heterocyclic nucleus containing from 5 to 6 atoms in the heterocyclic ring; each L represents a methine linkage; R_1, R_2 and R_3 each represents an alkyl group, an alkylene group joined to a methine linkage, or an aryl group; Q represents the non-metallic atoms required to complete a heterocyclic ketomethylene nucleus containing from 5 to 6 atoms in the heterocyclic ring; *m* represents an integer of from 1 to 5; *d, n* and *j* each represents an integer of from 1 to 2; *k* represents an integer of from 1 to 3; and, X represents an acid anion; and

(b) a complex of silver with an alkane or cycloalkane containing from 5 to 20 carbon atoms in which from 2 to 6 —CH_2— groups, but not more than one half the total number of —CH_2— groups, are replaced with a divalent sulfur or selenium atom; coating said emulsion on a support; and, bathing said emulsion in an aqueous ammoniacal hypersensitizing bath.

11. The method of spectrally sensitizing a photographic silver bromoiodide emulsion which comprises heating for 5 to 10 minutes, at 40 to 60° C. a methanolic solution containing the sensitizing dyes 3,3'-diethylselenodicarbocyanine salt; anhydro - 1 - ethyl-3-(3-sulfobutyl)thia-2'-cyanine salt and, a complex of silver with 1,10-dithia-4,7, 13,16-tetraoxacyclooctadecane; coating said emulsion on a support; and, bathing said emulsion for 2 to 3 minutes in an ammoniacal bath consisting essentially of 2 parts of 28% aqueous ammoniacal solution and 100 parts water, said bath being maintained at about 5° C. during hypersensitization.

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