

1

3,706,569

SILVER HALIDE EMULSION CONTAINING SILVER ETHYNYLCYCLOPENTANOL COMPLEX TO REDUCE DESENSITIZATION OF OPTICAL SENSITIZING DYE INCORPORATED THEREIN

Paul B. Gilman, Jr., and Jon D. Bass, Rochester, N.Y., assignors to Eastman Kodak Company, Rochester, N.Y.
No Drawing. Filed Dec. 4, 1970, Ser. No. 95,420
Int. Cl. G03c 1/08

U.S. Cl. 96—134 R

11 Claims

ABSTRACT OF THE DISCLOSURE

Light-sensitive photographic silver halide emulsions are provided which contain (1) a photographic spectral sensitizing dye having a polarographic cathodic halfwave potential more positive than about -1.80 volts, said dye being employed in the emulsion at a concentration which results in at least about $0.3 \log E$ desensitization of a test portion of the emulsion, when the test portion of the emulsion is coated on a support, sensitometrically exposed and developed for 6 minutes at 20°C . in Kodak D-19 developer; and (2) an organic silver complex in an amount effective to reduce the desensitization caused by the spectral sensitizing dye. Photographic emulsions in accordance with this invention exhibit higher speeds in the spectrally sensitized region (i.e., higher minus blue speeds) than prior art emulsions containing lower concentrations of spectral sensitizing dye. In addition, use of the higher dye concentrations in accordance with the present invention results in emulsions which exhibit sensitivity to longer wavelength radiation than prior art emulsions having lower dye concentrations.

This invention relates to photographic emulsions and more particularly to reducing the desensitization caused by photographic spectral sensitizing dyes.

It is known in the art of making photographic emulsions that various dyes such as polymethine dyes, extend the spectral sensitivity of photographic silver halide emulsions. However, spectral sensitizing dyes generally decrease the inherent blue sensitivity of silver halide emulsions. For each spectral sensitizer an optimum amount of dye for a particular emulsion must be determined by experimentation, and this amount is usually much less than monolayer coverage. Photographic spectral sensitizing dyes have previously been added to negative, developing-out silver halide emulsions in amounts which cause less than $0.3 \log E$ desensitization.

Glafkides, *Photographic Chemistry*, volume 2, published by Fountain Press, London, 1960, states at page 922 that desensitization by dyes, such as phenosafranine, is reduced by the presence of silver ions (i.e., low pAg); and, points out at page 906 that the sensitivity of infrared plates is increased by hypersensitizing, such as by bathing in silver nitrate. However, Glafkides fails to suggest any means for effectively using photographic spectral sensitizing dyes in concentrations which would, without some special treatment or addenda, cause more than $0.3 \log E$ desensitization.

Kuwabara in *Bull. Soc. Sci. Phot. of Japan*, No. 16, December 1966, suggests the use of acetylenic compounds as stabilizers in silver halide emulsions containing spectral sensitizing dyes, but does not suggest that high, desensitizing concentrations of spectral sensitizing dyes could be used with such acetylenic compounds.

Jones in U.S. Pat. 2,816,029, issued Dec. 10, 1957, states in column 1 that spectrally sensitized silver halide emulsions can be "hypersensitized" by increasing the silver ion concentration, but notes at column 1, lines 36 and 37, that such emulsions have poor keeping qualities.

2

Tani in *Phot. Sci. and Eng.* volume 13, No. 5, September and October 1969, page 236, refers to the reduction of desensitization caused by phenosafranine (a "desensitizing" dye) when the emulsion is prepared at low pAg. Tani does not suggest any means for employing sensitizing dyes in high concentrations which normally would desensitize negative silver halide emulsions.

One object of this invention is to reduce the amount of intrinsic blue desensitization caused when high concentrations of photographic spectral sensitizing dyes are added to photographic silver halide emulsions.

Another object of this invention is to provide a method of increasing the efficiency of the spectral sensitization of photographic silver halide emulsions.

A further object of this invention is to provide a method of using high levels of photographic spectral sensitizing dyes in photographic silver halide emulsions.

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

In accordance with one embodiment of this invention, light-sensitive photographic silver halide emulsions are provided which contain (1) a photographic spectral sensitizing dye having a polarographic cathodic halfwave potential more positive than about -1.80 volts, said dye being employed in the emulsion at a concentration which results in at least about $0.3 \log E$ desensitization of a test portion of the emulsion, when the test portion of the emulsion is coated on a support, sensitometrically exposed and developed for 6 minutes at 20°C . in Kodak D-19 developer; and (2) an organic silver complex in an amount effective to reduce the desensitization caused by the spectral sensitizing dye.

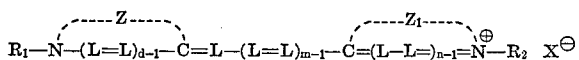
Photographic emulsions in accordance with this invention exhibit higher speeds in the spectrally sensitized region (i.e., higher minus blue speeds) than prior art emulsions containing lower concentrations of spectral sensitizing dye. In addition, use of the higher dye concentrations in accordance with the present invention results in emulsions which exhibit sensitivity to longer wavelength radiation than prior art emulsions having lower dye concentrations.

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 have a polarographic cathodic halfwave potential more positive than about -1.80 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 0.005 molar in acetic acid using a carbon paste or 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. Pats. 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 high concentrations in accordance with this invention have the following general formula:

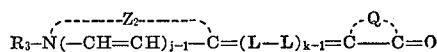


wherein d and n each represents a positive integer of from 1 to 2, m represents a positive integer of from 1 to 5, each L represents a methine group (e.g., $-\text{CH}=\text{C}(\text{CH}_3)=$, etc.), and Z and Z_1 each represents the non-metallic atoms necessary to complete a heterocyclic nucleus containing 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-phenyl-oxazole, 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-dialkyl naphth[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 -sulfoethyl, δ -sulfoethyl, 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'-diethylthiazolocarbo-cyanine iodide
- 3,3'-diethyl-4,4'-diphenylthiazolocarbo-cyanine iodide
- 3,3'-diethyl-9-methylthiacarbocyanine iodide
- 1,3,3'-triethylbenzimidazolo-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'-diethylthiadibocarbocyanine 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-sulfo-butyl)-benzimidazolocarbo-cyanine hydroxide
- Anhydro-5,6-dichloro-1-ethyl-3-(3-sulfoethyl)-3'-(3-sulfoethyl)-4',5'-benzobenzimidazolothiacarbocyanine hydroxide
- 1,1',3,3'-tetraethyl-naphth[1,2-d]imidazolocarbo-cyanine iodide
- Anhydro-5,6-dichloro-1,3-diethyl-(3'-sulfoethyl)-benzimidazoloselenacarbocyanine hydroxide
- 1,2-diethylthia-4'-carbocyanine iodide
- Anhydro-5,5',6,6'-tetrachloro-1,1'-diethyl-3,3'-di(4-sulfoethyl)-benzimidazolocarbo-cyanine 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-allyl-rhodanine, etc. 3-carboxyalkylrhodanines, e.g., 3-(2-carboxyethyl)rhodanine, 3-(4-carboxybutyl)rhodanine, etc., 3-sulfoalkylrhodanines, e.g., 3-(2-sulfoethyl)rhodanine, 3-(3-sulfoethyl)rhodanine, 3-(4-sulfoethyl)rhodanine, etc., or 3-arylrhodanines, e.g., 3-phenylrhodanine, etc., a 2(3H)-imidazo[1,2-a]pyridine nucleus; a 5,7-dioxo-6,7-dihydro-5-thiazolo[3,2-a]pyrimidine nucleus, e.g., 5,7-di-

5

oxo-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)-oxazolidinedione series) e.g., 3-ethyl-2-thio-2,4-oxazolidinedione, 3-(2-sulfoethyl)-2-thio - 2,4-oxazolidinedione, 3-(4-sulfoethyl)-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-2,5thiazolidinedione nucleus (i.e., the 2-thio-2,5-(3H,4H)-thiazolidinedione 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 - sulfoethyl) - 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 - imidazolidinedione, 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, Q₁ and Q₂ 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'-diethylselenadibocyanine 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'-tetraethylbenzimidazolcarbocyanine chloride
Anhydro-5,5',6,6'-tetrachloro-1,1'-diethyl-3,3'-di(3-sulfo-butyl)benzimidazolcarbocyanine hydroxide
Anhydro-5,5',6,6'-tetrachloro-1,1',3-triethyl-3'-(3-sulfo-butyl)-benzimidazolcarbocyanine hydroxide
5,5'-dichloro-3,3'-diethyl-9-phenylselenacarbocyanine iodide
3,3',9-triethyl-5,6,5',6'-dibenzothiacarbocyanine p-toluene-sulfonate

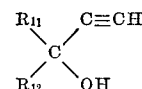
If desired, combinations of photographic spectral sensitizing dyes can be employed in the practice of the invention.

In accordance with this invention, photographic spectral sensitizing dyes are employed in concentrations which would normally cause at least 0.3 log E desensitization in the emulsion in which the dye is incorporated. The amount of dye which will cause 0.3 log E desensitization can be determined by adding various amounts of dye to a test portion of the emulsion, coating the emulsion on a support, sensitometrically exposing the emulsion and developing for 6 minutes at 20° C. in Kodak D-19 developer. For some dyes, such as various dicarbocyanine and tricarbocyanine dyes which typically extend spectral sensitivity to

6

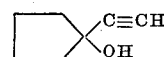
infrared radiation, optimum concentrations have previously been about 3 to 10 mg. of dye per mole of silver halide. High concentrations, such as 100 to 200 mg. per mole of silver, of dyes of this type have previously caused at least more than 0.3 log E desensitization. Infrared sensitizers generally have E_c values more positive than -1.0, such as -0.2 to -0.9, and E_a values more negative than about +0.6, such as +0.2 to +0.6. Infrared sensitizers sensitize silver halide to radiation longer than about 700 nm. Other photographic spectral sensitizing dyes, such as certain cyanine and merocyanine dyes, have been used in concentrations of up to 200 mg. (or more) of dye per mole of silver halide without causing 0.3 log E desensitization. These dyes can be effectively used at still higher concentrations in accordance with this invention. This invention allows monolayer dye coverage of the silver halide grains. Dye concentrations higher than monolayer coverage appear to exhibit no advantage over monolayer concentrations.

A variety of organic silver complexes can be used in emulsions to reduce the desensitization caused by high concentrations of photographic sensitizing dyes. The most useful organic silver complexes are complexes of silver with an alkyne which preferably contains from about 5 to 15 carbon atoms. Especially good results are obtained using complexes of silver with a 1-alkyne-3-ol. Preferred 1-alkyne-3-ol compounds which form useful silver complexes have the following formula:



wherein R₁₁ and R₁₂, taken separately, each represents a phenyl group (including substituted phenyl such as chlorophenyl) or an alkyl group (which can be substituted) of from 1 to 6 carbon atoms, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, tert.-butyl, n-amyl, tert.-amyl and n-hexyl, or R₁₁ and R₁₂, taken together, represent the atoms required to complete a cycloalkyl group containing from 4 to 6 carbon atoms, such as cyclobutyl, cyclopentyl or cyclohexyl.

An especially suitable silver alkyne complex is the silver complex of 1-ethynylcyclopentanol of the formula:



Also useful are complexes of silver with (1) carboxy-alkyl-substituted thiazolinethiones, such as 5-carbethoxy-4-methyl-3-carboxymethyl-4-thiazoline-2-thione; and (2) aromatic sulfonic acids such as p-toluenesulfonic acid.

Suitable silver complexing agents which can be employed in the practice of the invention include:

- (1) 1-ethynylcyclohexanol
- (2) 3-methyl-1-butyn-3-ol
- (3) 3-methyl-1-pentyn-3-ol
- (4) 1-hexyn-3-ol
- (5) 2-propynyl cyclohexylcarboxylate
- (6) 4-t-butyl-1-ethynylcyclohexanol
- (7) methyl propiolate
- (8) 3,5-dimethyl-1-hexyn-3-ol
- (9) 4-(1-hydroxy-2-propynyl)cyclohexene
- (10) 3-cyclopropyl-1-butyn-3-ol
- (11) 3-phenyl-1-propyn-3-ol
- (12) 3-(4-chlorophenyl)-1-butyn-3-ol

The organic silver complex is added to the emulsion in an amount sufficient to effectively reduce desensitization caused by the higher concentration of spectral sensitizing dye. The actual amount added depends primarily on the specific spectral sensitizing dye or dyes being used and the pAg of the emulsion. The most useful results are obtained when the organic silver complex is added in a sufficient concentration to lower the pAg of the emulsion from about 8.5 to about 3.0 to 7.0. Emulsions are normally

prepared at a pAg of about 7.5 up to 9. (Note that pAg values given herein are determined at 40° C.)

The organic silver complexes employed in this invention lower the pAg of the emulsion, but do not cause the intolerable fog and instability which results when the pAg of the emulsion is lowered with silver nitrate.

In view of the unique method of spectrally sensitizing a silver halide emulsion with a potentially desensitizing dye, the concentration of dye and the optimum pAg must be determined for each sensitizing dye. The concentration of sensitizing dye varies over a wide range, such as from about 0.001 g. to 3.5 g. per mole of silver in the emulsion, depending on the particular dye being used. As indicated above, the dyes can be used in concentrations which give monolayer coverage of the silver halide crystals. It is preferred that the dye be incorporated in the silver halide emulsions at a temperature ranging from 40° C. to 60° C. and that the organic silver complex be added to the emulsion prior to coating.

However, if desired, a gel layer imbibed in an ethanol solution of an organic silver complex, for example the silver complex of ethynylcyclopentanol, can be brought into contact with a coating containing a higher concentration of a potential desensitizing dye; the laminated element is then exposed, separated and processed in a typical photographic developer. Substantial speed gains can be obtained by this method. Similar results are obtained without harmful increases in minimum density when the gelatin layer is imbibed with a solution containing a silver salt of p-toluensulfonic acid or a silver complex of a thiazolinethione such as 5-carbethoxy-4-methyl-3-carboxymethyl-4-thiazoline-2-thione. Although speed increases are obtained using gelatin layers imbibed with a developer, such as Kodak D-19 developer, or a 1% silver nitrate solution, exposure and development must be carried out promptly to avoid instability and high fog. Prompt exposure and development are not required when organic silver complexes are utilized.

The process of this invention is useful in spectrally sensitizing any of the photographic silver halide emulsions, 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, agar-agar, gum arabic, alginic acid, polyvinyl alcohol, polyvinyl pyrrolidone, cellulose esters, 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. Pats. 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, allylthiocyanate, 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. Pat. 2,540,086, issued Feb. 6, 1951), potassium chloropalladate (Stauffer et al. U.S. Pat. 2,598,079, issued May 27, 1952), etc., or mixtures of such sensitizers; antifoggants such as ammonium chloroplati-

nate (Trivelli et al. U.S. Pat. 2,566,245, issued Aug. 28, 1951), ammonium chloroplatinate (Trivelli et al. U.S. Pat. 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 non-spectrally sensitized control coating is prepared as follows. To 243 ml. of a 5 percent aqueous gelatin solution is added 72 g. of a gelatin fine-grain silver bromide emulsion containing 80 g. gelatin per mole of silver and weighing 1.65 kilograms per mole of silver. The liquid emulsion is held for 15 minutes at 40° C., adjusted to a pAg of 8.5 using a solution of dimethylformamide containing 5 percent by weight of silver ethynylcyclopentanol, adjusted to a pH of 6.5, combined with a surfactant and a hardener and coated on a gelatin subbed polyethylene terephthalate support at 0.004 inch. The dried coatings are exposed in a wedge spectrograph for ¼ second at 1.0 mm. slit width and developed in Kodak D-19 developer at 20° C. for 2 minutes. The element is assigned a relative blue speed at 400 nm. of 100 and has a minimum density of 0.04.

EXAMPLE 2

A spectrally sensitized control coating is prepared as follows. The procedure set out in Example 1 is followed with the exception that 1.5 ml. of a methanol solution containing 0.1% by weight of 3,3'-diethyl-9,11,15,17-dineopentylene thiapentacarbocyanine iodide (I) is added to the emulsion at a level of 180 mg. dye per mole of silver. The pAg is then adjusted in the same manner as described in Example 1. The exposed and processed element has a blue speed relative to Example 1 of 0.78 at 400 nm. (which amounts to a 2.10 log *E* speed loss) and no spectral sensitivity at 1,000 nm. with a minimum density of 0.04.

EXAMPLES 3-7

Five elements are prepared as described in the procedure set out in Examples 1-2 with the exception that a prescribed amount of the dimethylformamide solution of the silver ethynylcyclopentanol complex is added to the liquid emulsion melt to lower the pAg of the final melt.

Table I lists the example number, the pAg of the melt and the relative blue speed at 400 nm. and the infrared speed at 1,000 nm. Processing is the same as in Example 1.

TABLE I

Supersensitization of a Far Infrared Dye (1,000 nm.)

Ex.	Format	pAg	D _{min.}	Relative speed at—	
				400 nm.	1,000 nm.
1	Control, no dye	8.5	.04	100	0
2	180 mg. Dye I/mole Ag	8.5	.04	.78	0
3	do	7.9	.04	.78	0
4	do	7.0	.04	1.56	0
5	do	5.6	.04	6	0.02
6	do	4.9	.17	100	0.10
7	do	4.5	.48	100	0.04

NOTE.—Dye I=3,3'-diethyl-9,11,15,17-dineopentylene thiapentacarbo-cyanine iodide. (The optimum concentration of this dye has previously been from about 1 to 5 mg. per mole of silver halide in emulsions having a pAg of about 8.5.)

These data, listed in Table I, show that:

(a) 180 mg. Dye I/mole Ag causes a 2.10 log *E* desensitization in the intrinsic blue sensitivity of the silver bromide emulsion,

(b) by lowering the pAg to 4.9 with the silver ethynylcyclopentanol complex, the intrinsic blue speed of the emulsion is regained,

(c) a 0.39 log *E* speed increase in spectral sensitivity at 1,000 nm. is observed, and

(d) only a slight increase in minimum density (+0.13) is realized.

EXAMPLES 8-14

These examples illustrate the invention using a dicarbo-cyanine dye. The procedure set out in Examples 1-7 is followed with the exception that 3,3'-diethylselenadicarbo-cyanine iodide (II) is substituted for Dye I in the emulsion melt. The results are shown in Table II.

TABLE II

Supersensitization of an Infrared Dicarbo-cyanine Dye (700 nm.)

Ex.	Format	pAg	D _{min.}	Relative speed at—	
				400 nm.	700 nm
8	Control, no Dye	8.5	.05	100	-----
9	180 mg. dye II/mole Ag	8.5	.05	3	-----
10	do	7.9	.04	4	-----
11	do	7.0	.04	14	1
12	do	5.8	.04	27	6
13	do	4.9	.20	55	6
14	do	4.5	.20	100	12

NOTE.—Dye II=3,3'-diethylselenadicarbo-cyanine iodide, *E*_a=-0.84; *E*_s=+0.46. (The optimum concentration of this dye has previously been about 5 to 10 mg. per mole of silver halide in emulsions having a pAg of about 8.5.)

These data, entered in Table II, demonstrate once again that by using an organic silver complex in an emulsion melt which contains a dye at a concentration that strongly desensitizes the emulsion, one cannot only regain the intrinsic blue speed of the emulsion but also obtain a re-

spectable increase in spectral sensitivity in the region that the dye absorbs without an intolerable increase in minimum density. Undesirably high minimum densities of over 1.0 are obtained when silver nitrate is substituted for organic silver complex to obtain a similar pAg.

EXAMPLES 15-21

These examples illustrate the invention using a merocarbocyanine dye. The procedure set out in Examples 1-7 is followed with the exception that 1,3-diethyl-5-[4-(3-ethyl-2-benzothiazolynylidene)-2-butenylidene]-2-thio-barbituric acid (III) is substituted for Dye I in the emulsion melt. The results are tabulated in Table III.

TABLE III

Supersensitization of an Infrared Merodicarbocyanine Dye (700 nm.)

Ex.	Format	pAg	D _{min.}	Relative speed at—	
				400 nm.	700 nm.
15	Control, no dye	8.4	.04	100	-----
16	180 mg. Dye III/mole Ag	8.4	.04	14	6
17	do	8.0	.04	14	12
18	do	7.0	.05	27	25
19	do	6.0	.04	100	100
20	do	5.0	.04	100	60
21	do	4.0	.05	100	12

NOTE.—Dye III=1,3-diethyl-5-[4-(3-ethyl-2-benzothiazolynylidene)-2-butenylidene]-2-thio-barbituric acid. (The optimum concentration of this dye is about 5 to 10 mg. per mole of silver halide in emulsions having a pAg of about 8.5.)

The sensitometric results listed in Table III show that:

(a) 180 mg. Dye III causes a 0.90 log *E* desensitization in the intrinsic blue sensitivity (400 nm.) of the silver bromide emulsion (Example 15 versus Example 16),

(b) by lowering the pAg to 6.0 (Example 19) with the organic silver complex, the blue speed of the emulsion is regained,

(c) a 2.40 log *E* speed increase in spectral sensitivity is observed, and

(d) no increase in minimum density, is realized.

Thus, as seen in the above Examples 1-21, it is possible, through the use of an organic silver complex to make use of concentrations of a pentacarbo-cyanine dye (far infrared), a dicarbo-cyanine dye (red) or a merodicarbo-cyanine dye which drastically desensitizes photographic silver halide emulsions at a normal coating pAg of 8.5.

EXAMPLES 22-23

The procedure which is set out in Examples 1-7 is followed with the exception that the following individual dyes are substituted for Dye I in the emulsion at three different concentrations and at pAg's ranging from 9-5 and the coatings are exposed to a graduated density sensitometric step wedge. The pAg once again is regulated by the addition of a silver ethynylcyclopentanol complex. The results are tabulated in Table IV.

TABLE IV

Example	Dye (mg./m. Ag)	pAg	Relative blue speed	Relative minus blue speed	Relative clear speed range (nm).	Spectral sens.
22	None (control)	9.0	100	-----	-----	-----
23	IV (50)	9.0	68	100	100	520-630
24	IV (450)	9.0	-----	-----	-----	560-620
25	IV (450)	8.0	49	46	41	500-640
26	IV (450)	7.0	78	204	148	490-650
27	IV (450)	6.0	257	631	427	490-660
28	IV (450)	5.0	468	1,410	1,020	490-670

NOTE.—Dye IV=3,3'-diethylthiacarbocyanine chloride (*E*_a=+0.78 v.; *E*_s=-1.0 v.).

TABLE V

Example	Dye (mg./m. Ag)	pAg	Relative blue speed	Relative minus blue speed	Relative clear speed range (nm).	Spectral sens.
29	None (control)	9.0	100	-----	-----	-----
30	V (200)	8.0	49	100	100	530-660
31	V (400)	9.0	-----	-----	-----	580-660
32	V (400)	8.0	15.5	69	68	520-660
33	V (400)	7.0	101	759	631	500-670
34	V (400)	6.0	276	1,590	1,050	490-670
35	V (400)	5.0	302	1,590	1,380	490-680

NOTE.—Dye V=5,5'-dichloro-3,3',9-triethylthiacarbocyanine bromide (*E*_a=+0.87 v.; *E*_s=-1.06 v.).

11

The data in Tables IV and V show the tolerable amount of desensitization (loss of blue speed) when typical photographic spectral sensitizing dyes are employed at near optimum concentrations in emulsions coated at a conventional pAg of about 8.0 to 9.0 (Examples 23 and 30). However, higher concentrations of the dye result in substantial (more than .3 log *E*) desensitization (Examples 24 and 32).

EXAMPLES 36-42

The procedure which is set out in Examples 1-7 is followed with the exception that a silver bromiodide emulsion is used in place of the silver bromide emulsion and anhydro-5,5',6,6'-tetrachloro-1,1',3-triethyl-3'-(3-sulfo-butyl)benzimidazolocarbo-cyanine hydroxide (Dye VI) is substituted for Dye I. The pAg once again is regulated by the addition of a silver ethynylcyclopentanol complex. The results are tabulated in Table VI.

TABLE VI

Example	Dye (mg./m. Ag)	pAg	Relative speed at—	
			400 nm.	580 nm.
36	None (control)	8.5	100	100
37	VI (385)	8.5	100	100
38	VI (775)	8.5	100	100
39	VI (1,550)	8.5	75	100
40	VI (2,325)	8.5	13	13
41	VI (3,100)	8.5	100	100
42	VI (3,100)	3.0	100	200

NOTE.—Dye VI=Anhydro-5,5',6,6'-tetrachloro-1,1',3-triethyl-3'-(3-sulfo-butyl)benzimidazolocarbo-cyanine hydroxide ($E_a=+0.52$ v.; $E_c=-1.50$ v.).

In accordance with the present invention, addition of an organic silver complex effectively reduces the desensitization caused by the higher dye concentration. Use of higher dye concentrations results in higher clear speeds and higher speeds in the region of spectral sensitivity (minus blue speeds) than emulsion containing optimum dye concentrations but no organic silver complex. Generally similar results are obtained with other photographic spectral sensitizing dyes, including all of those referred to above. Also, generally similar results are obtained with other organic silver complexes, such as silver and *p*-toluenesulfonic acid complexes or complexes of silver with 5-carbethoxy-4-methyl-3-carboxymethyl-4-thiazoline-2-thione.

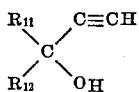
The invention has been described in detail with particular reference to preferred embodiments thereof, but, it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

We claim:

1. A light-sensitive photographic silver halide emulsion containing

(a) a photographic spectral sensitizing methine dye having a polarographic cathodic halfwave potential more positive than about -1.80 volts, said dye being employed in said emulsion at a concentration which results in at least about $0.3 \log E$ desensitization of a test portion of said emulsion, when said test portion of said emulsion is coated on a support and sensitometrically exposed and developed for 6 minutes at 20°C . in Kodak D-19 developer; and,

(b) an organic silver complex in an amount effective to reduce the desensitization caused by said dye, said complex having the following formula:



wherein R_{11} and R_{12} , taken separately, each represents phenyl or an alkyl group containing from 1 to 6 carbon atoms and, taken together, R_{11} and R_{12} represents the atoms required to complete a cyclo-alkyl group containing from 4 to 6 carbon atoms.

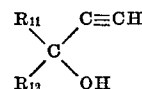
2. A light-sensitive photographic silver halide emulsion containing

(a) a photographic spectral sensitizing cyanine or

12

merocyanine dye having a polarographic cathodic halfwave potential more positive than about -1.80 volts, said dye being employed in said emulsion at a concentration which results in at least about $0.3 \log E$ desensitization of a test portion of said emulsion, when said test portion of said emulsion is coated on a support and sensitometrically exposed and developed for 6 minutes at 20°C . in Kodak D-19 developer; and,

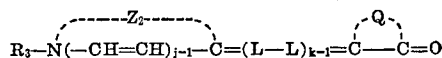
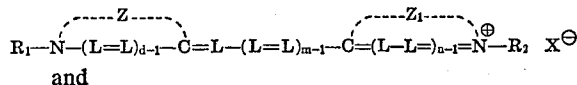
(b) an organic silver complex in an amount effective to reduce the desensitization caused by said dye, said complex having the following formula:



wherein R_{11} and R_{12} , taken separately, each represents phenyl or an alkyl group containing from 1 to 6 carbon atoms and, taken together, R_{11} and R_{12} represent the atoms required to complete a cyclo-alkyl group containing from 4 to 6 carbon atoms.

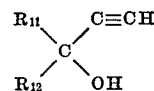
3. A light-sensitive photographic silver halide emulsion containing

(a) a photographic spectral sensitizing dye having a polarographic cathodic halfwave potential more positive than about -1.80 volts, said dye being employed in said emulsion at a concentration which results in at least about $0.3 \log E$ desensitization of a test portion of said emulsion, when said test portion of said emulsion is coated on a support and sensitometrically exposed and developed for 6 minutes at 20°C . in Kodak D-19 developer, said 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 6; 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) an organic silver complex in an amount effective to reduce the desensitization caused by said dye, said complex having the following formula:



wherein R_{11} and R_{12} , taken separately, each represents phenyl or an alkyl group containing from 1 to 6 carbon atoms and, taken together, R_{11} and R_{12} represent the atoms required to complete a cyclo-alkyl group containing from 4 to 6 carbon atoms.

4. The photographic emulsion defined in claim 4 wherein said dye is an infrared sensitizing dye which has a cathodic polarographic halfwave potential between about -0.2 and -0.9 volts and an anodic polarographic halfwave potential between about $+0.2$ and $+0.6$ volts, and sensitizes the emulsion to radiation longer than 700 nm .

5. A light-sensitive photographic silver halide emulsion containing about 400 mg. per mole of silver of 3,3'-diethylthiacarbocyanine chloride, said emulsion containing a sufficient amount of silver ethynylcyclopentanol com-

13

plex to lower the pAg of the emulsion from 8.5 to about 5.0 to 6.0.

6. A light-sensitive photographic silver halide emulsion containing

(a) 3,3'-diethyl-9,11,15-17-dineopentylene thiapentacarbocyanine salt, said dye being employed at a concentration which results in at least about 0.3 log *E* desensitization of a test portion of said emulsion, when said test portion of said emulsion is coated on a support and sensitometrically exposed and developed for 6 minutes at 20° C. in Kodak D-19 developer; and,

(b) a silver ethynylcyclopentanol complex in an amount effective to reduce the desensitization caused by said dye.

7. A light-sensitive photographic silver halide emulsion containing

(a) 3,3'-diethylselenadecarbocyanine salt, said dye being employed at a concentration which results in at least about 0.3 log *E* desensitization of a test portion of said emulsion, when said test portion of said emulsion is coated on a support and sensitometrically exposed and developed for 6 minutes at 20° C. in Kodak D-19 developer; and,

(b) a silver ethynylcyclopentanol complex in an amount effective to reduce the desensitization caused by said dye.

8. A light-sensitive photographic silver halide emulsion containing

(a) 1,3-diethyl-5-[4-(3-ethyl-2-benzothiazolinyldiene)-2-butenylidene]-2-thiobarbituric acid, said dye being employed at a concentration which results in at least about 0.3 log *E* desensitization of a test portion of said emulsion, when said test portion of said emulsion is coated on a support and sensitometrically exposed and developed for 6 minutes at 20° C. in Kodak D-19 developer; and,

(b) a silver ethynylcyclopentanol complex in an amount effective to reduce the desensitization caused by said dye.

9. A light-sensitive photographic silver halide emulsion containing

(a) 3,3'-diethylthiacarbocyanine salt, said dye being employed at a concentration which results in at least about 0.3 log *E* desensitization of a test portion of said emulsion, when said test portion of said emul-

14

sion is coated on a support and sensitometrically exposed and developed for 6 minutes at 20° C. in Kodak D-19 developer; and,

(b) a silver ethynylcyclopentanol complex in an amount effective to reduce the desensitization caused by said dye.

10. A light-sensitive photographic silver halide emulsion containing

(a) 5,5'-dichloro-3,3',9-triethylthiacarbocyanine salt, said dye being employed at a concentration which results in at least about 0.3 log *E* desensitization of a test portion of said emulsion, when said test portion of said emulsion is coated on a support and sensitometrically exposed and developed for 6 minutes at 20° C. in Kodak D-19 developer; and

(b) a silver ethynylcyclopentanol complex in an amount effective to reduce the desensitization caused by said dye.

11. A light-sensitive photographic silver halide emulsion containing

(a) anhydro-5,5',6,6'-tetrachloro-1,1',3-triethyl-3'-(3-sulfobutyl)benzimidazolocarbo-cyanine hydroxide, said dye being employed at a concentration which results in at least about 0.3 log *E* desensitization of a test portion of said emulsion, when said test portion of said emulsion is coated on a support and sensitometrically exposed and developed for 6 minutes at 20° C. Kodak D-19 developer; and

(b) a silver ethynylcyclopentanol complex in an amount effective to reduce the desensitization caused by said dye.

References Cited

UNITED STATES PATENTS

3,212,900 10/1965 Oguchi et al. 96—109

OTHER REFERENCES

Kuwabara: Bull. Soc. Sci. Phot. of Japan, No. 16, December 1966.

NORMAN G. TORCHIN, Primary Examiner

W. H. LOUIE, Jr., Assistant Examiner

U.S. Cl. X.R.

96—109 R