# Millikan et al.

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[54]	PHOTO	GRAPHIC MATERIALS
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[56]	TIN	References Cited
	Ur	IITED STATES PATENTS
		1958 Knott 96/127
,		1971 Hiller 96/130
2,597	,856 /	1952 Damschroder 96/108
	T-1	

2,642,361	/1953	Damschroder et al 96/10	8
2,448,060	/1948	Smith et al 96/10	
2,540,085	/1951	Baldsiefen 96/10	8

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## [57] ABSTRACT

Light-sensitive silver halide grains having an average size of up to 0.2 micron are sensitized with a noble metal sensitizer at a concentration of at least 50 mg. noble metal per mole of silver, and a sulfur sensitizer at a weight ratio of sulfur to noble metal of about 1:15 to 1:75; said silver halide grains being spectrally sensitized with a photographic spectral sensitizing methine dye.

20 Claims, No Drawings

## PHOTOGRAPHIC MATERIALS

This invention relates to photographic materials, and more particularly to fine grain silver halide photographic materials.

The combination of noble metal sensitizers and sulfur sensitizers has been suggested in the prior art for photographic silver halide emulsions. Typical disclosures of such sensitizers are made by Smith et al. in U.S. Pat. No. 2,448,060 isused Aug. 31, 1948, 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 Damschroder et al. U.S. Pat. No. 2,642,361 issued June 16. 1953. Hiller in U.S. Pat. application Ser. No. 3,573,920, and corresponding to Belgian Pat. No. 724,740 of Dec. 31, 1969, describes spectrally sensitized fine grain silver halide emulsions and states that such emulsions can be sensitized with sulfur and gold sensitizers. However, none of these references, nor any 20 other reference known to applicants, suggest the sensitization of fine grain silver halide emulsions with a high concentration of noble metal sensitizer together with a low concentration of sulfur sensitizer.

Previously, it had been assumed that noble metal sen- 25 sitization was most effective with large silver halide grains. Glafkides, Photographic Chemistry, published by the Fountain Press, London, 1958, states at page 320 that gold sensitization is mainly effective with large silver halide grains, which have higher sensitivity to 30 light than fine silver halide grains (i.e., up to 0.2 micron in size). Glafkides also states at page 319 that gold sensitization frequently results in substantial increases in fog and causes emulsion instability, which often results in the emulsion becoming useless after being kept for 35 a few days.

Fine grain silver halide emulsions must be used instead of faster large grain silver halide emulsions for various purposes, for example in photographic applications where high resolution is essential, such as holography and microphotography. Hence, it appears highly desirable to provide stable emulsions comprising fine silver halide grains which have low fog and high speeds.

One object of this invention is to provide photographic silver halide grains which exhibit increased speed to blue radiation.

Another object of this invention is to provide chemically sensitized photographic silver halide emulsions which are stable and exhibit increased speed to blue radiation.

A further object of this invention is to provide photographic silver halide emulsions which are particularly useful in applications requiring high resolving power, such as holography and microphotography.

Still another object of this invention is to provide 55 spectrally sensitized photographic silver halide emul-

Another object of this invention is to provide spectrally sensitized fine grain silver halide emulsions having higher speeds in the region of spectral sensitivity.

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

In accordance with this invention, light-sensitive silver halide grains having an average grain size up to about 0.2 micron are sensitized with the combination of a noble metal sensitizer, at a concentration of about at least 50 milligrams noble metal per mole of silver, and a sulfur sensitizer at a weight ratio of sulfur to noble metal of about 1:15 to 1:75; and, the silver halide grains are spectrally sensitized with a photographic spectral sensitizing methine dye.

The combination of a high concentration of noble metal sensitizer and a low concentration of sulfur sensitizer, together with a photographic spectral sensitizing dye, results in substantial and unexpected speed increases in the region of inherent sensitivity of silver halide grains. The increase in inherent sensitivity is accomplished without causing high fog or emulsion instability.

Silver halide grains employed in the practice of this invention can comprise silver chloride, silver bromide, 757,789 filed Sept. 5, 1968 now U.S. Pat. No. 15 silver bromoiodide, silver chlorobromoiodide or mixtures thereof. The silver halide grains can range in size up to 0.2 micron, and preferably up to 0.15 or 0.1  $\mu$ m. Grains in the range of about 0.02 up to 0.09 micron give excellent results. Such silver halide grains can be prepared by any of the well-known procedures. Very fine grain emulsions known in the art as "Lippmann" emulsions are useful herein.

The noble metal sensitizers useful in this invention include the well-known gold sensitizers and other noble metals such as palladium and platinum, including any of the noble metal sensitizers described in Smith et al U.S. Pat. No. 2,448,060 issued Aug. 31, 1948. Typical useful gold sensitizers are described in Waller et al U.S. Pat. No. 2,399,083 issued Apr. 23, 1946, Baldesiefen U.S. Pat. Nos. 2,540,085 and 2,540,086 both issued Feb. 6, 1951; Damschroder U.S. Pat. No. 2,597,856 issued May 27, 1952 and Damschroder et al. U.S. Pat. No. 2,642,361 issued June 16, 1953. Illustrative addenda suitable for furnishing the noble metal moiety in accordance with this invention include:

gold chloride potassium aurate, potassium auriaurite, potassium auricyanide, potassium aurithiocyanate, gold sulfide, gold selenide, gold iodide. potassium chloroaurate. ethylenediamine-bis-gold chloride,

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ammonium chloropalladate, i.e., (NH<sub>4</sub>)<sub>2</sub>PtCl<sub>4</sub>, ammonium chloropalladate, i.e., (NH<sub>4</sub>)<sub>2</sub>PdCl<sub>6</sub>; and organic gold sensitizers having the formulas:

The noble metal sensitizer is employed in accordance with the invention in a concentration of from at least about 50 milligrams of noble metal per mole of silver, and preferably from about 125 to 175 milligrams noble metal sensitizer per mole of silver. Note that concentrations of noble metal are expressed in terms of noble metal and are not based on the total weight of the compound containing the noble metal. The noble metal sensitizer is employed at concentrations lower than which causes substantial fog, such as fog levels over 3. Generally, there is no advantage in employing over 200 mg. noble metal per mole of silver.

CiH;

CH5

In accordance with the invention, the silver halide grains are chemically sensitized with a sulfur sensitizer. Sulfur sensitizers are well known in the art and are described, for example, by Damschroder et al. U.S. Pat. No. 2,642,361 issued June 16, 1953, columns 3 and 4. Typical sulfur sensitizers contain a = C = S group or a -C-

S-S-C- group. Typical sulfur sensitizers are thiourea, allylisothiocyanate, thiosinamine (allylthiourea), cystine and β-ethyl xanthate propionic acid. Also useful are methyl or ammonium thiocyanates, such as alkali
5 metal thiocyanates (e.g., sodium or potassium thiocyanate) or alkaline earth metal thiocyanates (e.g., calcium thiocyanine, strontium thiocyanate, etc.), cadmium thiocyanate and ammonium thiocyanate. Especially useful are the alkali metal thiosulfates, preferably
10 sodium or potassium thiosulfate, or ammonium thiosulfate. Thioureas, such as those referred to above, also produce particularly useful results.

Sulfur sensitizers are employed herein at a weight ratio of sulfur to noble metal of about 1:15 to 1:75, and preferably about 1:30 to about 1:50. The amount of labile sulfur, not the entire weight of the compound containing the labile sulfur, is used in calculating the useful concentrations of sulfur. As will be apparent to those skilled in the art, certain sulfur sensitizers (e.g., sodium those sulfur atoms is labile. These compounds are used in concentrations calculated on the basis of the one labile sulfur atom therein.

Any methine (including polymethine) photographic spectral sensitizing dye can be employed in the practice of this invention. The most useful methine dyes are the cyanine, merocyanine, hemicyanine and hemioxonol dyes. The dyes can be used in widely varying concentrations, with optimum concentrations being determined by any suitable means previously described in the art. Generally, about 100 to 2,000 mg. dye per mole of silver provide good results, although larger or smaller amounts produce useful results depending on the particular dye and silver halide used.

Typical useful cyanine dyes 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, such as used in cyanine dyes, which nuclei can contain a second hetero atom such as oxygen, sulfur, selenium or nitrogen, such as the following nuclei: a thiazole nucleus, e.g., 4-phenylthiazole, 4-methylthiazole, thiazole, 5-phenyl-thiazole, 4,5methylthiazole, 4,5-diphenylthiazole, 4-(2dimethylthiazole, thienyl)thiazole, benzothiazole, 4-cholorbenzothiazole, 6-chlorobenzothiazole, 5-chlorobenzothiazole, 4-methylbenzothiazole, chlorobenzothiazole, 5-6-methyl-benzothiazole, methylbenzothiazole, 6-bromobenzothiazole, bromobenzothiazole, phenylbenzothiazole, 6-phenylbenzothiazole, 4-math-5-methoxybenzothiazole, 6oxybenzothiazole, 6methoxybenzothiazole, 5-iodobenzothiazole, 4-ethoxybenzothiazole, iodobenzothiazole, tetrahydrobenzothiazole, 5.6ethoxybenzothiazole, dimethoxy benzothiazole, 5,6-dioxymethylenebenzobenzothiazole, 5-hydroxy thiazole, hydroxybenzothiazole, naphtho[2,1-d]thiazole, naph-

tho[1,2-d]thiazole, 5-methoxynaphtho[2,3-d]thiazole, 5-ethoxynaphtho[2,3-d]thiazole, methoxynaphtho[2,3-d]thiazole, methoxynaptho[2,3-d]thiazole, 4'-methoxythianaphtheno-7',6'-4,5-thiazole, etc.; an oxazole nucleus, e.g., 5 4-methyloxazole, 5-methyloxazole, 4-phenyloxazole, 4,5-diphenyloxazole, 4-ethyloxazole, dimethyloxazole, 5-phenyloxazole, benzoxazole, 5chlorobenzoxazole, 5-methylbenzoxazole, phenylbenzoxazole, 6-methylbenzoxazole, 5,6-dime- 10 thylbenzoxazole, 4,6-dimethylbenzoxazole, methoxybenzoxazole, 5-methoxybenzoxazole, 5-6-methoxybenzoxazole, chlorobenzoxazole. 6-hydroxybenzoxazole, naphhydroxybenzoxazole, tho[2,1-d]oxazole, naptho[1,2-d]-oxazole, etc.; a 15 selenazole nucleus, e.g., 4-methylselenazole, phenylselenazole, benzoselenazole, chlorobenzoselenazole, 5-methoxybenzoselenazole, 5-hydroxybenzoselenazole, tetrahydrobenzoselenazole, naphtho[2,1-d]selenazole, naphtho[1,2-d]selenazole, etc.; a thiazoline nucleus, e.g., thiazoline, 4-methylthiazoline, etc.; a pyridine nucleus, e.g., 2-pyridine, 5-methyl-2-pyridine, 4-pyridine, 3-methyl-4-pyridine, etc.; a quinoline nucleus, e.g., 2quinoline, 3-methyl-2-quinoline, 5-ethyl-2-quinoline, 6-chloro-2-quinoline, 8-chloro-2quinoline, 6-methoxy-2-quinoline, 8-ethoxy-2-quinoline, 8-hydroxy-2quinoline, 4-quinoline, 6-methoxy-4-quinoline, 7-methyl-4-quinoline, 8-chloro-4-quinoline, 1- 30 isoquinoline, 3,4-dihydro-1-isoquinoline, isoquinoline, etc; a 3,3-dialkylindolenine nucleus, e.g., 3,3-dimethylindolenine, 3,3,5-trimethylindolenine, etc.; and, an imidazole nucleus, e.g., imidazole, 1alkylimidazole, 1-alkyl-4-phenylimidazole, 1-alkyl-4,5- 35 dimethylimidazole, benzimidazole, alkylbenzimidazole, 1-aryl-5,6-dichlorobenzimidazole, 1-alkyl-1H-naphtho[1,2-d]imidazole, 1-aryl-3Hnaphtho[1,2-d]imidazole, 1-alkyl-5-methoxy-1Hnaphtho[1,2-d]imidazole, etc.; X represents an acid 40 anion, such as chloride, bromide p-toluene sulfonate. methane sulfonate, methylsulfate, ethylsulfate, perchlorate, etc.; R<sub>1</sub> and R<sub>2</sub> each represents an alkyl group (including substituted alkyl) having from 1 to 18, and preferably one to four carbon atoms, such as methyl, 45 ethyl, propyl, isopropyl, butyl, sec-butyl, hexyl, dodecyl, octadecyl, benzyl, β-phenylethyl, sulfoalkyl such as  $\beta$ -sulfoethyl,  $\gamma$ -sulfopropyl,  $\gamma$ -sulfobutyl,  $\delta$ -sulfobutyl, etc.; carboxyalkyl such as β-carboxyethyl, γ-carboxypropyl, δ-carboxybutyl, etc.; sulfatoalkyl such as γ-sul- 50 foatopropyl and δ-sulfatobutyl, 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 R2, such as dyes containing the betaine type structure. Some specific cyanine dyes that can be used 55 in the process of this invention include the following: 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'-diphenylthiazolocarbocyanine iodide

3,3'-diethyl-9-methylthiacarbocyanine iodide 1,3,3'-triethylbenzimidazolo-oxacarbocyanine iodide 5-chloro-1,3,3'-triethylbenizimidazolo-oxacarbocyanine iodide

5,6-dichloro-1,3,3'-triethylbenzimidazolothiacarbocyanine iodide

1,1',3-triethylbenzimidazolo-2'-carbocyanine iodide 1,1',3-triethylbenzimidazolo-40'-carbocyanine iodide 1,1'-diethyl-2,4'-carbocyanine iodide

0 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-b1-ethyl-3-(3-sulfobutyl)-3'-(3-sulfopropyl)-4',5'-benzobenzimidazolothiacarbocyanine hydroxide

1,1,',3,3'-tetraethyl-naphtho[1,2-0 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(4-5 sulfobutyl)benzimidazolocarbocyanine hydroxide

Especially useful cyanine dyes include the carbocyanine, dicarbocyanine and tricarbocyanine dyes. Cyanine dyes which have at least one nucleus selected from a 5- or 6-dichlorobenzimidazole nucleus, a 5- or 6-methoxy-substituted benzothiazole nucleus or a 5- or 6-trifluoromethylbenzimidazole nucleus provide particularly good results. Supersensitization of these dyes with a sulfonated polynuclear aromatic organic supersensitizer, an azaindene or a silver halide reducing agent (e.g., those described below) is sometimes advantageous.

A particularly useful class of cyanine dyes are tricarbocyanine dyes in which the meso carbon atom of the methine linkage of the dye is attached to the nitrogen atom of an amino group which forms an enamine with the methine linkage of the tricarbocyanine dye. The term "tricarbocyanine" denotes dyes having the ammidinium-ion chromophoric system (see Mees and James, *The Theory of the Photographic Process*, Third Edition, 1966, page 201). Typically, such dyes have two nitrogen-containing heterocyclic nuclei which are joined by a straight chain methine linkage having seven methine groups. The carbon atom of the central methine group of the methine linkage is referred to herein as the meso carbon atom of the methine linkage.

The word "enamine" is used herein to refer to the group

$$C=C-N$$

See Advances in Organic Chemistry, Methods and Results, Volume 4, Raphael, Taylor and Wynberg, 1963, Interscience, page 3, and Fieser and Fieser, Advanced Organic Chemistry, Reinhold Publishing Corp., 1961, pages 494-499.

The preferred enamine tricarbocyanine dyes used herein have the following formula:

wherein a and b each represents an integer of from 1 to 2; X<sub>1</sub> represents an acid anion, such as those mentioned above; R<sub>3</sub> and R<sub>4</sub> each represents a value given for  $R_1$  and  $R_2$  above;  $Z_2$  and  $Z_3$  are each selected from a value given for Z and Z<sub>1</sub> above; Q<sup>1</sup> represents a diva-5 lent linkage, such as ethylene, trimethyl, orthophenylene, which linkage can be substituted, for example, with halogen, an alkyl or an alkoxy group of one to four carbon atoms; and R<sub>5</sub> and R<sub>6</sub> taken separately each represents a member selected from the group consisting of 10 XXII alkyl and aryl, and, taken together R<sub>5</sub> and R<sub>6</sub> represent the non-metallic atoms required to complete a heterocyclic ring containing from 5 to 6 atoms, e.g., a morpholino group, a thiomorpholino group, a piperidino group, a piperazinyl group, (preferably a 4-alkyl-1- 15 piperazinyl group such as methyl, ethyl, ethoxycarbonyl, propyl or butyl groups, or an 4-aryl-1-piperazinyl group such as a 4-phenyl-1-piperazinyl group) a pyrrolidinyl group, an indolinyl group, a tetrahydroquinoyl group and a decahydroquinoyl group. Especially good 20 results are obtained when Z<sub>2</sub> and Z<sub>3</sub> each represents a benzoxazole, a naphthothiazole nucleus, or a benzothiazole nucleus; Q1 represents an ethylene linkage; and, R<sub>5</sub> and R<sub>6</sub> are taken together and represents a piperazinyl group, 4-ethoxycarbonyl-1-piperazinyl being pre- 25

Typical specific enamine tricarbocyanine dyes useful in the practice of this invention are set out in Table A below:

### TABLE A

I	11-(4-Ethoxycarbonyl-1-piperazinyl)-3,3'- diethyl-10,12-ethyleneoxatricarbocyanine
II	perchlorate 3,3'-Diethyl-10,12-ethylene-11-(4-methyl-1- piperazinyl)oxatricarbocyanine perchlorate
III	3,3'-Deithyl-10,12-ethylene-11-(4-methyl- lpiperazinyl)thiatricarbocyanine perchlorate
IV .	11-(4-Ethoxycarbonyl-1-piperazinyl)-3,3'- diethyl-10,12-ethylene-5,5'-diphenyloxa- tricarbocyanine perchlorate
<b>V</b>	Anhydro-11-(4-ethoxycarbonyl-1piperazinyl- 10,12- ethylene-3,3'-di(3-sulfopropyl)thiatricar-
	bocyanine hydroxide
VI	Anhydro-10,12-ethylene-11-(4-methyl- piperazinyl)-3,3'-di(3-sulfopropyl)oxa- tricarbocyanine hydroxide
VII	Anhydro-10,12-ethylene-11-(4-methyl-1- piperazinyl)-3,3'-di(3-sulfopropyl)thia- tricarbocyanine hydroxide
VIII	11-(4-Ethoxycarbonyl-1-piperazinyl)-3,3'- diethyl-10,12-ethylenethiatricarbocyanine perchlorate
IX	11-(4-phenyl-1-piperazinyl)-3,3'-diethyl-10, 12-orthophenylenethiatricarbocyanine p-toluene sulfonate
	Anhydro-11- dibutylamino-10, 12-ethylene-3,3'- di(3-sulfopropyl) thiatricarbocyanine hydroxide, soldium salt
XI_	3,3'-Diethyl-10,12-ethylene-11-(1- pyrrolidinyl)-thiatricarbocyanine iodide
XII	10,12-ethylene-1,1', 3,3,3', 3'-hexamethyl-11-(1-pyrrolidinyl)indo- tricarbocyanine iodide
XIII	3,3'-Diethyl-10,12-ethylene-11-piperidion- thiatricarbocyanine iodide
XIV	3,3'-Diethyl-10,12 -ethylene-1morpholinothiatricarbocyanine iodide
xv	3,3'-Diethyl-11-piperidino-10,12- trimethylenethiatricarbocyanine iodide
xvi	3,3'-Diethyl-10,12-ethylene-11-(1-1- idolinyl)oxatricarbocyanine perchlorate

XVII 3,3'-Diethyl-10,12-ethylene-11-[1,-(1,2,3,4tetrahydroquinolyl]oxyatricarbocyanine perchlorate XVIII 11-Diethylamine-3,3'diethyl-10,12-ethylenethriatricarbocyanine perchlorate 11-Diethylamino-10,12-ethylene-XIX 1,11,3,3',3'-hexamethylindrotricarbocyanine perchlorate 3,3'-Diethyl-10,12-ethylene-11-[1-(1,2,3,4-tetrahydroquinolyl)]4,5,',4',5'-dibenzothia-XXtricarbocyanine perchlorate 11-Diphenylamino-3,3'-diethyl-10,12-XXI ethyleneoxatricarbocyanine perchlorate 11-Dimethylamino-3,3'-diethyl-10,12ethylenethiatricarbocyanine perchlorate XXIII 3,3'-Diethyl-10,12-trimethylene-11thiomorpholinooxathiatricarbocyanine perchlorate 3,3'-Diethyl-10,12-ethylene-11 XXIV (1-decahydroquinoly)-4,4' tricarbocyanine perchlorate ΧXV Anhydro-11-(4-ethoxycarbonylpiperazin-1-yl)-10,12-ethylene-3,3'-bis(3-sulfopropyl)-5,6;5',6'-dibenzothiatricarbocyanine hydroxide, triethylamine slat

The enamine tricarbocyanine dyes employed in this invention can be prepared by reacting one mol of an intermediate having formula III below:

III. 
$$\begin{array}{c} O \\ N = (CH - CH)_{a-1} = C - CH = CH - N - C - CH_3 \\ R_3 & C_{aH_5} \\ X_1 \\ \end{array}$$

with one mol of an enamine salt of formula IV below:

to obtain a compound having formula V below:

40 V.

$$R_{5}$$
 $R_{6}$ 
 $N = (CH - CH)_{a-1} = C - CH = CH - C = C - CH_{5}$ 
 $X_{1} \ominus R_{5}$ 

One mol of the compound of formula V above can then be reacted with one mol of a compound having formula VI below:

50 VI. O CH<sub>2</sub>-C 
$$Z_1$$
  $E$   $X_1 \oplus X_1 \oplus X_2 \oplus X_1 \oplus X_2 \oplus X_2 \oplus X_3 \oplus X_4 \oplus X_5 \oplus X$ 

to obtain a compound having formula II above. In the above formulas, X<sub>1</sub>, a, b, Z<sub>2</sub>, Z<sub>3</sub>, Q<sup>1</sup>, R<sub>3</sub>R<sub>4</sub>, R<sub>5</sub> and R<sub>6</sub> have the meanings given above. The reactions are advantageously conducted in a suitable solvent, such as acetone or acetic anhydride, and preferably in the presence of a basic condensing agent, such as triethylamine, and at elevated temperatures, such as the refluxing temperature of the reaction mixtures. Further details on the preparation of dyes employed in this invention appear in Jeffreys U.S. Pat. application Ser. No. 314,864 filed Oct. 10, 1963 U.S. Pat. No. 3483195 and corresponding French Pat. No. 1,410,864; Jeffreys

U.S. Pat. application Ser. No. 518,010 filed Jan. 3, 1966 U.S. Pat. No. 3506655, and corresponding Belgian Pat. No. 674,800; Fumia et al. U.S. Pat. application Ser. No. 574,947 filed Aug. 25, 1966 Pat. No. 3482978 and corresponding Belgian Pat. No. 702,840; 5 and, Fumia et al. U.S. Pat. application Ser. No. 860,395 filed Sept. 23, 1969 now abandoned, and entitled "Sensitizing Dyes and Photographic Emulsions and Elements Containing Said Dyes," and continuation-in-part application thereof U.S. Pat. Ser. No. 22,708 filed Mar. 10 25, 1970 Pat. No. 3623881. Supersensitization of these dyes with a sulfonated polynuclear aromatic organic supersensitizer, an azaindene or a silver halide reducing agent is described by Hiller et al in U.S. Pat. application Ser. No. 860,394 filed Sept. 23, 1969 now abandoned. 15

Merocyanine dyes are effectively employed in the practice of this invention. Typical useful merocyanine dyes have the following formula:

VII. 
$$R_7 - N(-CH = CH)_{0-1} - C(=L-L)_{p-1} = C - C = 0$$

wherein R<sub>7</sub>, L and Z<sub>4</sub> represents a value selected from those given above for R<sub>1</sub>, L and Z, respectively; c represents an integer of from 1 to 2; p represents an integer 25 of from 1 to 3; and, Q represents the non-metallic atoms necessary to complete a 5- or 6-membered nucleus of the type used in merocyanine dyes typically containing a hetero atom selected from nitrogen, sulfur, selenium, and oxygen, such as a 2-pyrazolin-5-one 30 nucleus, e.g., 3-methyl-1-phenyl-2-pyrazolin-5-one, 1-phenyl-2-pyrazoline-5-one, 1-(2-benzothiazolyl)-3methyl-2-pyrazolin-5-one, etc.; an isoxazolone nucleus, 3-phenyl-5(4H)-isoxazolone, 3-methyl-5(4H) -isoxazolone, etc.; an oxindole nucleus, e.g., 1-alkyl-2- 35 oxindoles, etc.; a 2,4,6-triketohexahydropyrimidine nucleus, e.g., barbituric acid or 2-triobarbituric 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, 1,3diethyl, 1,3-dipropyl, 1,3-diisopropyl, 1,3-dicyclohexyl, 40 1,3-di( $\beta$ -methoxyethyl), etc.; or 1,3-diaryl (e.g., 1,3diphenyl, 1,3-di-(p-chlorphenyl), 1,3-di(p-ethoxycarbonylphenyl), etc.); or 1-aryl (e.g., 1-phenyl, 1-pchlorophenyl, 1-p-ethoxycarbonylphenyl), etc.) or 1-(e.g., 1-ethyl-3-phenyl, 1-n-heptyl-3-45 alkyl-3-aryl phenyl, etc.) derivatives; a rhodanine nucleus (i.e., 2-thio-2,4-thiazolidinedione series), such as rhodanine, 3-alkylrhodanines, 3-ethylrhodanine, e.g., allylrhodanine etc., 3-carboxyalkylrhodanines, e.g., 50 3-(2-carboxyethyl)rhodanine, 3-(4-carboxybutyl)-3-sulfoalkylrhodanines, rhodanine, etc., 3-(2-sulfoethyl)rhodanine, 3-(3-sulfopropyl)rhoda-3-(4-sulfobutyl)rhodanine, etc., arylrhodanines, e.g., 3-phenylrhodanine, etc., 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-(2sulfoethyl)-2-thio-2,4-oxazolidinedione, 3-(4sulfobutyl)-2-thio-2,4-oxazolidinedione, 3-(3carboxypropyl)-2-thio-2,4-oxazolidinedione, etc.; a 65 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 se-

ries), e.g., 3-ethyl-2-thio-2,5-thiazolidinedione, etc; a 2,4thiazolidione nucleus, e.g., 2,4-thiazolidinedione, 3-ethyl-2,4thiazolidione 3-phenyl-2,4-thiazolidinedione, 3-α-naphthyl-2,4thiazolidinedione, etc; a thiazolidinone nucleus, e.g., 4-thiazolidinone, 3-ethyl-4-thiazolidinone, 3-phenyl-4thiazolidinone, 3-α-naphthyl-4-thiazolidinone, etc; a 2-thiazolin-4-one nucleus, e.g., 2-ethylmercapto-2thiazolin-4-one, 2-alkylphenylamino-2-thiazolin-4-one, 2-diphenylamino-2-thiazolin-4-one, etc; a 2-imino-4oxazolidinone (i.e., pseudohydantoin) nucleus; a 2,4imidazolidinedione (hydantoin) nucleus, e.g., 2,4imidazolidinedione, 3-ethyl-2,4-imidazolidinedione, 3-phenyl-2,4-imidazolidinedione,  $3-\alpha$ -naphthyl-2,4imidazolidinedione, 1,3-diethyl-2,4imidazolidinedione. 1-ethyl-3-phenyl-2,4-1-ethyl-3-α-naphthyl-2,4imidazolidinedione, imidazolidinedione. 1,3-diphenyl-2,4imidazolidinedione, etc; a 2-thio-2,4-20 imidazolidinedione (i.e., 2-thiohydantoin) nucleus, e.g., 2-thio-2,4-imidazolidinedione, 3-ethyl-2-thio-2,4-3-(4-sulfobutyl)-2-thio-2,4imidazolidinedione, imidazolidinedione, 3-(2-carboxyethyl)-2-thio-2,4imidazolidinedione, 3-phenyl-2-thio-2,4-3-α-naphthyl-2-thio-2,4imidazolidinedione, 1.3-diethyl-2-thio-2,4imidazolidinedione. imidazolidinedione, 1-ethyl-3-phenyl-2-thio-2,4imidazolidinedione, 1-ethyl-3- $\alpha$ -naphthyl-2-thio-2,4imidazolidinedione, 1,3-diphenyl-2-thio-2,4imidazolidinedione, etc.; a 2-imidazolin-5-one nucleus, e.g., 2-propylmercapto-2-imidazolin-5-one, etc.; etc. (Especially useful are nuclei wherein Q represents the non-metallic atoms required to complete a heterocyclic nucleus containing five to six atoms in the heterocyclic ring, three to four of said atoms being carbon, and two of said atoms being selected from the group consisting of nitrogen, oxygen, and sulfur, and at least one of said two atoms being a nitrogen atom. Typical useful merocyanine dyes are described in Brooker et al. U.S. Pat. No. 2,493,747 and 2,493,748, both issued Jan. 10, 1950, and Knott U.S. Pat. No. 2,839,403 issued June 17, 1958.

Another preferred class of methine dyes include those comprising first and second nuclei joined by a double bond or methine linkage (including one or more methine groups); the first of said nuclei being selected from the groupd consisting of (1) a nitrogen-containing heterocyclic nucleus of the type used in cyanine dyes having from 5to 6 non-metallic atoms in the heterocyclic ring, and (2) a nitrogen-containing heterocyclic ketomethylene nucleus of the type used in merocyanine dyes having from 5 to 6 non-metallic atoms in the heterocyclic ring, joined in each instance by a carbon atom of (1) or (2) to said linkage; and said second nucleus being an enamine group selected from the group consisting of a 1-(3,4,4a,5,6,7-hexahydro-2-naphthyl)pyrrolidine group, a 1-(3,3a,4,5-tetrahydro-2H-inden-6-yl)pyroldine group, a 1-(2-nonbornylidene)pyrroline group and a 1-(1-indanylidene)pyrrolidine group, joined at a carbon atom thereof to said linkage, to complete said dye. Preferred dyes of this type include those represented by the following formulas:

VIII.  $\begin{array}{c} \bigoplus_{i=1}^{\ell} C(-L=L)_{i-i} - D & X_2 \\ \end{array}$ 

45

and

IX. 
$$Q_{-c} = C = L(-L = L)_{r-1}$$

wherein e and g represents a positive integer of from 1 to 2; f represents a positive integer of from 1 to 3; L represents a methine linkage, e.g., =CH-, =C(CH<sub>3</sub>), =C(C<sub>6</sub>H<sub>5</sub>), etc.; D represents an enamine group selected from a 2,3,4,4a,5,6-hexahydro-7-(1-pyr-10 rolidinyl)-1-naphthyl group, a 2,6,7,7a-tetrahydro-5-(1-pyrrolidinyl)-3-indenyl group, a 3-(1-pyrrolidinyl-2-norbornen-2-yl group or a 3-(1-pyrrolidinyl)-2-indenyl group, represented by the following basic structures:

and

which groups can be further substituted on appropriate nuclear carbon atoms thereof by alkyl, e.g., methyl, butyl, etc., or alkoxy, e.g., methoxy, butoxy, etc., and the like; R<sub>8</sub>, X<sub>2</sub> and Q<sub>1</sub> represents a value given above for R<sub>1</sub>, X and Q, respectively. Methine dyes of this type can be conveniently prepared in a number of ways. For example, a number of the dyes defined by formula VIII above are advantageously prepared by heating a mixture of (1) a heterocyclic salt of the formula:

X. 
$$R_{\delta} = N (= CH - CH)_{\bullet-1} = C - \left(L = L\right)_{\stackrel{\bullet}{t-1}} - N - C_{\bullet}H_{\delta}$$

$$R_{\delta} = N - C_{\bullet}H_{\delta}$$

wherein f is 2 or 3; e, L,  $R_8$ ,  $X_2$  and  $Z_5$  are as previously defined, and  $R_9$  represents a hydrogen atom or an acyl group, e.g., acetoxy, phenoxy, etc., with (2) an enamine intermediate selected from the group consisting of a 1(3,4,4a,5,6,7-hexahydro-2-naphthyl)pyrrolidine,

or a 1-(3,3a,4,5-tetrahydro-2H-inden-6-yl)pyrrolidone, or a 1-(2-norbornylidene)pyrrolidinium salt, e.g., the chloride, bromide, iodide, perchlorate, p-toluenesulfonate, etc. salt, or a 1-(1-indanylidene)pyrrolidinium salt, e.g., the chloride, bromide, iodide, perchlorate, p-toluenesulfonate, etc. salt, in approximately equimolar proportions, in a solvent medium such as ethanol, pyridine, N,N-dimethylacetamide, acetic anhydride, etc. Advantageously, a basic condensing agent such as triethylamine is used with the acetic anhydride reaction medium. The dyes are then separated from the reaction mixtures and purified by one or more recrystallizations from appropriate solvents such as methanol, mixtures of pyridine and methanol, and the like. The dyes 15 wherein the value of f is 1 in formula VIII above are advantageously prepared with (1) a heterocyclic salt of the formula:

20 XI. 
$$R_8 = N(=CH-CH)_{g-1} = C-SR_{10}$$

wherein g, R<sub>8</sub>, X<sub>2</sub> and Z<sub>5</sub> are as previously defined and R<sub>10</sub> represents an alkyl or aryl group, e.g., methyl, butyl, phenyl, etc., and (2) an enamine intermediate above defined, under generally similar reaction conditions and purification of the dyes as described in the preceding procedure. The dyes defined by formula IV above are also prepared by the above procedure described for the dyes of formula VIII using the same enamine intermediates except that the heterocyclic salt of formula X is replaced by a ketomethylene heterocyclic compound of the formula:

XII. 
$$O = \stackrel{\cdot}{C} - \stackrel{\cdot}{C} = L(-L = L)_{\mathfrak{g}-1} - N - C_{\theta}H_{\delta}$$

wherein g, L, R<sub>9</sub> and Q<sub>1</sub> are as previously defined. Dyes of this type are described in Fumia et al. U.S. Pat. application Ser. No. 830,483 filed June 4, 1969, and include dves as 3-ethyl-2such {2-[2,3,4,4a,5,6-hexahydro-7-(1-pyrrolidinyl)-1naphthyl]vinyl} benzoxazolium iodide; 3-ethyl-2-{2-[2,3,4,4a,-5,6-hexahydro-7-(1-pyrrolidinyl)-1naphthyllvinyl} benzothiazolium iodide; 3-ethyl-5-{[2,3,4,4a,5,6-hexahydro-7-(1-pyrrolidinyl)-1naphthyl]methylene} rhodanine; 3-ethyl-2-[2,6,7,7atetrahydro-5-(1-pyrrolidinyl)-3-indenyl]benzoperchlorate; 3-ethyl-2thiazolium  $\{2-[2,6,7,7a-\text{tetrahydro-}5-(1-\text{pyrrolidinyl})-3$ indenyl]-vinyl} benzoxazolium iodide; 3-ethyl-2-{2-[2,6,7,7a-tetrahydro-5-(1-pyrrolidinyl)-3indenyl]vinyl} benzothiazolium iodide; 3-phenyl-4-{[2,6,7,7a-tetrahydro-5-(1 pyrrolidinyl)-3-indenyl]methylene} -2-isoxazolin-5-one; 3-methyl-1-phenyl-4-{[2,6,7,7a-tetrahydro-5-(1-pyrrolidinyl)-3--2pyrazolin-5-one; 3-ethyl-5indenyl]methylene} {[2,56,7,7a-tetrahydro-5-(1-pyrrolidinyl)-3indenyl]methylene} rhodanine; 3-ethyl-2-2-norbornen-2-yl]vinyl {2-[3-(1-pyrrolidinyl)-{benzoxazolium perchlorate; 3-ethyl-2- 2-[3-(1 pyrrolidinyl)-2-norbornen-2-yl]vinyl}benzothiazolium perchlorate; 1-ethyl-2-{2-[3-(1-pyrrolidinyl)-2-norbornen-2-yl]vinyl}

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perchlorate; naphthoj 1,2-d thiazolium {2-[3-(1-pyrrolidinyl)-2-indenyl]vinyl}trimethyl-2-3H-indolium perchlorate: 3-ethvl-2-{2-[3-(1-pyrrolidinyl)-2-indenyl]vinyl}-3-ethyl-2- 5 benzoxazolium perchlorate; {2-[3-(1-pyrrolidinyl)-2-indenyl]vinyl}

perchlorate benzothiazolium and {2-[3-(1pyrrolidinyl)-2-indenyl]vinyl}

1-ethyl-2-

naphtho[1,2-d]thiazolium perchlorate.

Another highly useful class of dyes are enamine 10 methine dyes which contain a double bond remote from the chromophoric chain. Such useful enamine dyes include cyanine, hemicyanine and hemioxonol dyes. Such dyes can have formula II above wherein R<sub>5</sub> and R<sub>6</sub>, taken separately, each represents an allyl 15 group, or R<sub>5</sub> and R<sub>6</sub>, taken together, represent the atoms required to complete a 1,2,5,6-tetrahydro-1pyridyl nucleus or a 3-pyrrolin-1-yl nucleus. Other dyes of this class include those represented by formulas VIII and IX above wherein D represents a group having one 20 of the following formulas:

CH: CH: -CN -CH=CH CH=CH-CH

Still other useful dyes of this class have the following formula:

XIII.

wherein  $Q_2$  represents a value selected from those given for Q<sub>1</sub> above and D<sub>1</sub> represents a group having the following formula:

Enamine dyes containing a double bond remote from the chromophoric chain can be prepared in a manner similar to the preparation of the enamine dyes of formulas II, VIII and IX above, but using one of the following starting materials:

Intermediate A - 1-cyclopentylidene-3-pyrrolinium perchlorate

3-Pyrrolinium perchlorate (17.0 g) and 3-pyrroline (4 drops) are suspended in ethanol (75 ml) and the suspension heated on a steam bath to obtain a solution. Cyclopentanone (10.1 g) is then added to the hot solution and solid precipitated. The mixture is heated to reflux and then chilled. The solid is collected on a filter and the yield is 22.5 g (95 percent), m.p. =  $202^{\circ}-203^{\circ}$ 

Intermediate B — 1-Isopropylidene-3-pyrrolinium perchlorate

A solution of 3-pyrroline (14.5 g) in ether (1.1) is treated with 72 percent perchloric acid (28.0 g) with 30 stirring and cooling. Decanted, stirred residue with a fresh portion of ether (1 l.), decanted and then suspended the residue in ethanol (125 ml). Acetone (11.6 g) is added, the mixture is heated to reflux and then chilled. The solid is collected on a filter and then re-35 crystallized from ethanol. The yield is 28 g (67 percent), m.p. = 168°-169° C dec. In preparing dyes from this compound, it is necessary to have acetic anhydride present which indicates that the compound may be a hydrate.

40 Intermediate C Cyclopentenylidenediallylammonium perchlorate

Cyclopentanone (25.2 g), diallylamine (49.0 g), ptoluene sulfonic acid (0.5 g) and benzene (90 ml) are placed in an apparatus designed for the continuous removal of water and heated at reflux for 16 hours. After evaporation under reduced pressure, the residue is distilled in vacuum to yield the enamine (b.p. ~93° C/15 mm Hg). The enamine so obtained is dissolved in ether (1 l.), and the cooled solution treated with 72 percent perchloric acid until the mixture is just acid. Decanted, stirred residue with a fresh portion of ether (1 l.), decanted and then recrystallized the solid from ethanol. The yield is 42.8 g (54 percent), m.p. = 122°-123° C dec.

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Intermediate D - 1-(5,5-Dimethyl-3-methylene-1cyclohexen- 1-yl)-3-pyrroline

Isophorone (41.4 g), 3-pyrroline (31.0 g), p-toluene sulfonic acid (0.5 g) and benzene (90 ml) are placed in an apparatus designed for the continuous removal of water and heated at reflux for 1 hour. After evaporat- 15 230°-231° C dec. ing under reduced pressure, the residue is distilled in vacuum. Decomposition takes place during the distillation with 12.1 g (21 percent) of the desired material being obtained. (b.p. =  $89^{\circ}$ - $95^{\circ}$  C/0.4-1.1mm Hg) Intermediate E - 5,5-Dimethyl-3-(3-pyrrolin-1-yl)-2- 20 butadienyl]-benzoxazolium perchlorate cyclohexen-1-one

5,5-Dimethyl-1,3-cyclohexanedione (28.0 g), pyrroline (15.2 g) and benzene (250 ml) are placed in an apparatus designed for the continuous removal of water and heated at reflux for 1 hour. The mixture is then evaporated, under reduced pressure, to a volume  $^{35}$ of ~100 ml. The residue is diluted to ~400 ml with ligroine (b.p. 35°-60°) and the mixture chilled. The solid is collected on a filter and the yield is 37.5 g (96 percent), m.p. = 111°-112° C. dec.

Intermediate F - 1-(3-Chloro-5,5-dimethyl-2-40 cyclohexen-1-ylidene-3-pyrrolinium perchlorate

To a solution of 5,5-dimethyl-3-(3-pyrrolin-1-yl)-2cyclohexen-1-one (37.5 g) in benzene (300 ml) is added phosphorous pentachloride (40.8 g). The mixture is heated to reflux and then removed from heat until the initial reaction has subsided. The reaction is then heated at reflux for 2 % hours. After cooling, the mixture is stirred with ice water (~300 ml). The water layer is removed and an aqueous solution of sodium perchlorate (36 g/~100 ml) is added to it. After chilling, the solid is collected on a filter and dried. The crude yield is 40.5 g (67 percent). After one recrystallization from ethanol, the yield is 29.5 g (49 percent),  $m.p. = 140^{\circ}-141^{\circ} C dec.$ 

1-Cyclopentylidene-1,2,5,6-Intermediate G tetrahydropyridinium perchlorate

1,2,5,6-Tetrahydropyridine (8.7 g) and cyclopenta-10 none (10.7 g) are dissolved in ethanol (25 ml) and the solution treated with 72 percent perchloric acid (14.0 g) with cooling. The mixture is then heated at reflux for 15 minutes and, after chilling, the solid is collected on a filter. The yield is 16.6 g (66 percent), m.p. =

Representative useful enamine dyes having a double bond remote from the chromophoric chain, and the preparation thereof, are given below:

3-Ethyl-2-[4-(3-pyrrolin-1-yl)-3,4-trimethylene-1,3-

1-Cyclopentylidene-3-pyrrolinium perchlorate (1.3 g), 2-(2-acetanilidovinyl)-3-ethylbenzoxazolium iodide (2.2 g), and triethylamine (1.5 ml) are dissolved in acetic anhydride (15 ml) and stirred at room temperature for 15 minutes. The solid is collected on a filter and, after two recrystallizations from methanol, the yield of purified dye is 0.5 g (25 percent), m.p. =  $262^{\circ}$ - $263^{\circ}$  C

3,3'-Diethyl-10,12-ethylene-11-(3-pyrrolin-1-yl)oxatricarbocyanine perchlorate

45
$$50 \bigcirc CH - CH = CH - CH = CH - CH_{\bigoplus} C_{1H_{i}} Clo_{i}^{\ominus}$$

1-Cyclopentylidene-3-pyrrolinium perchlorate (1.2 g), 2-(2-acetanilidovinyl)-3-ethylbenzoxazolium iodide (4.8 g), and triethylamine (1.5 ml) are dissolved in acetic anhydride (15 ml) and heated at reflux for 10 minutes. After cooling to room temperature, the solid is collected on a filter, washed with methanol and then recrystallized from cresol/methanol. The yield of purified dve is 0.5 g (22 percent), m.p. =  $267^{\circ}$ - $268^{\circ}$  C dec. 3-Ethyl-2-[4-(3-pyrrolin-1-yl)-1,3-pentadienyl]benzoxazolium perchlorate

1-Isopropylidene-3-pyrrolinium perchlorate (2.3 g), 2-(2-acetanilidovinyl)-3-ethylbenzoxazolium iodide (4.3 g), acetic anhydride (1.0 ml) and triethylamine 10 (1.7 ml) are dis-solved in ethanol (20 ml) and heated at reflux for 10 minutes. After chilling, the solid is collected on a filter and then recrystallized from methanol. The yield of purified dye is 1.1 g (29 percent), m.p. = 223°-224° C dec.

3-Methyl-2-[4-(3-pyrrolin-1-yl)-1,3-pentadienyl]thiazolium perchlorate

1-Isopropylidene-3-pyrrolinium perchlorate (2.3 g), 2-(2-anilinovinyl)-3-methyl-2-thiazolium iodide (3.5 g), acetic anhydride (2.0 ml), and triethylamine (3.4 20 ml) are dissolved in acetonitrile (20 ml) and heated at reflux for 10 minutes. After chilling, the solid is collected on a filter and then recrystallized from methanol. The yield of purified dye is 1.2 g (36 percent), m.p. = 223°-224° C dec.

2-[2-(2-Diallylamino-1-cyclopentenyl)vinyl]-3-ethylbenzothiazolium perchlorate

Cyclopentenylidenediallylammonium perchlorate (2.9 g), 2-(2-acetanilidovinyl)-3-ethylbenzothiazolium iodide (4.5 g) and triethylamine (1.4 ml) are dissolved in acetonitrile (15 ml) and heated at reflux for 5 minutes. After chilling, the crude dye is collected on a filter and recrystallized from methanol with the methanol solution being treated with norite. The yield of purified dye is 1.47 g (33 percent), m.p. = 219°-220° C dec. 11-Diallyamino-3,3'-diethyl-10,12-ethyleneoxatricar-bocyanine perchlorate

Cyclopentenylidenediallylammonium perchlorate (1.32 g), 2-(2-acetanilidovinyl)-3-ethylbenzoxazolium iodide (4.56 g) and triethylamine (1.5 ml) are dissolved in N,N-dimethylacetamide (10 ml) and heated at a gentle reflux for 5 minutes. The reaction mixture is diluted to ~300 ml with boiling methanol and, after chilling, the dye is collected on a filter (0.97 g, 32 percent). After one recrystallization from methanol, the yield of purified dye is 0.64 g (21 percent), m.p. = 229-230° C dec.

5-(2-Diallylamino-1-cyclopentenyl)methylene-3ethylrhodanine

5-Acetanilidomethylene-3-ethylrhodanine (3.06 g), cyclopentenylidenediallylammonium perchlorate (2.64 g) and triethylamine (1.5 ml) are dissolved in N,N-dimethylacetamide (15 ml) and heated at a gentle reflux for 5 minutes. The reaction mixture is diluted to 300 ml with boiling methanol and, after chilling, the dye is collected on a filter. The yield is 0.40 (12 percent), m.p. = 127°-128° C dec.

3-Ethyl-2-[4,6-neopentylene-6-(3-pyrrolin-1-yl)-1,3,5-hexatrienyl]benzothiazolium iodide

1-(5,5-Dimethyl-3-methylene-1-cyclohexen-1-yl)-3-pyrroline (1.0 g) and 2-(2-acetanilidovinyl)-3-ethylbenzothiazolium iodide (2.3 g) are dissolved in ethanol (15 ml) and heated at reflux for 5 minutes. After chilling, the solid is collected on a filter and dried. The crude yield is 1.4 g (56 percent). After one recrystallization from methanol, the yield of purified dye is 1.1 g (44 percent), m.p. = 233°-234° C dec. 1,3,3-Trimethyl-2-[4,6-neopentylene-6-(3-pyrrolin-1-

1-(5,5-Dimethyl-3-methylene-1-cyclohexen-1-yl)-3-pyrroline (1.0 g) and 2-(2-acetanilidovinyl)-1,3,3-trimethyl-3H-indolium iodide (2.2 g) are dissolved in ethanol (15 ml) and heated at reflux for 5 minutes. An aqueous solution of sodium perchlorate (1.0 g/ $\sim$ 5 ml) is added and, after chilling, the crude dye is collected on a filter. After one recrystallization from methanol, the yield of purified dye is 0.5 g (21 percent), m.p. = 231°-232° C dec.

yl)-1,3,5-hexatrienyl]-3H-indolium perchlorate

3-Ethyl-5-[3,5-neopentylene-5-(3-pyrrolin-1-yl)-2,4-pentadienylidene]rhodanine

5-Acetanilidomethylene-3-ethylrhodanine (3.1 g) and 1-(5,5-dimethyl-3-methylene-1-cyclohexen-1-yl)-3-pyrroline (2.1 g) are dissolved in N,N-dimethylacetamide (15 ml) and heated at a gentle reflux for 5 minutes. After diluting with  $\sim 300$  ml of boiling methanol, the mixture is allowed to stand at room temperature for 30 minutes and then the dye is collected on a filter. The yield is 1.0 g (28 percent), m.p. = 219°-220° C dec.

3-Ethyl-5-[5,5-dimethyl-3-(3-pyrrolin-1-yl)-2-cyclohexenylidene]-rhodanine

1-(3Chloro-5,5-dimethyl-2-cyclohexen-1-ylidene)-3-pyrrolinium perchlorate (3.10 g), 3-ethylrhodanine (1.61 g) and triethylamine (3.1 ml) are dissolved in ethanol (20 ml) and heated at reflux for 10 minutes. 25 After chilling, the solid is collected on a filter and then recrystallized from pyridine/methanol. The yield of purified dye is 1.78 g (53 percent), m.p. = 192°-193° C dec.

3-Allyl-5-[5,5-dimethyl-3-(3-pyrrolin-1-yl)-2-cyclohexenyli-dene]rhodanine

3-Allylrhodanine (1.73 g), 1-(3-chloro-5,5-dimethyl-2-cyclohexen-1-ylidene)-3-pyrrolinium perchlorate (3.10 g) and triethylamine (3.1 ml) are dissolved in ethanol (20 ml) and heated at reflux for 1 minute. The mixture is allowed to stand at room temperature for 30 minutes and then the crude dye is collected on a filter. After one recrystallization from pyridine/methanol, the yield of purified dye is 2.36 g (68 percent), m.p. = 202°-203° C dec.

5-[5,5-Dimethyl-3-(3-pyrrolin-1-yl)-2-cyclohexenylidene]-3-ethyl-1-phenyl-2-thiohydantoin

1-(3-Chloro-5,5-dimethyl-2-cyclohexen-1-ylidene)-3-pyrrolinium perchlorate (3.10 g), 3-ethyl-1-phenyl-2-thiohydantoin (2.2 g) are triethylamine (3.1 ml) are

dissolved in ethanol (15 ml) and heated at reflux for 10 minutes. After chilling, the crude dye is collected on a filter and then recrystallized from methanol. The yield of purified dye is  $1.50 \, \text{g}$  (38 percent), m.p. =  $219^{\circ}$ - $220^{\circ}$  C dec.

3-Ethyl-2-[4-(1,2,5,6-tetrahydro-1-pyridyl)-3,4-trimethylene-1,3-butadienyl]benzoxazolium perchlo-

1-Cyclopentylidene-1,2,5,6-tetrahydropyridinium perchlorate (2.7 g), 2-(2-acetanilidovinyl)-3-ethylbenzoxazolium iodide (4.3 g) and triethylamine (1.5 ml) are dissolved in acetic anhydride (20 ml) and stirred at room temperature for 2 hours. The crude dye is collected on a filter and then recrystallized from methanol. The yield of purified dye is 0.9 g (21 percent), m.p. = 214°-215° C dec.

3-Ethyl-2-[4-(1,2,5,6-tetrahydro-1-pyridyl)-3,4-30 trimethylene-1,3-butadienyl]benzothiazolium perchlorate

1-Cyclopentylidene-1,2,5,6-tetrahydropyridinium perchlorate (2.7 g), 2-(2-acetanilidovinyl)-3-ethylbenzothiazolium iodide (4.5 g) and triethylamine (1.5 ml) are dissolved in acetic anhydride (20 ml) and the mixture stirred at room temperature for 1 ¼ hours. The crude dye is collected on a filter, rinsed with ethanol and then recrystallized twice from methanol. The yield of purified dye is 1.0 g (23 percent), m.p. = 227°-228° C dec.

3,3'-Diethyl-10,12-ethylene-11-(1,2,5,6-tetrahydro-1-pyridyl)-oxatricarbocyanine perchlorate

1-Cyclopentylidene-1,2,5,6-tetrahydropyridinium perchlorate (1.2 g), 2-(2-acetanilidovinyl)-3-ethylben-zoxazolium iodide (4.8 g) and triethylamine (1.5 ml) are dissolved in acetic anhydride (20 ml) and heated at reflux for 5 minutes. The hot mixture is turned into a beaker, srred for 2 minutes and the solid then collected on a filter. After one recrystallization from N,N-dimethylacetamide, the yield of purified dye is 1.1 g (37 percent), m.p. = 251°-252° C dec. 3-Ethyl-5-[2-(3-pyrrolin-1-yl)-1-cyclopentenylme-

thylene]-rhodanine

Cyclopentylidene-3-pyrrolinium perchlorate (2.36 10 g), 5-acetanilidovinyl-3-ethylrhodanine (3.06 g), and triethylamine (1.5 ml) are dissolved in ethanol (15 ml) and heated at reflux for 5 minutes. After chilling, the crude dye is collected on a filter and, after one recrystallization from benzene, the yield of purified dye is 15 1.35 g (44 percent), m.p. =  $199^{\circ}-200^{\circ}$  C dec. 3-Carboxymethyl-5-[2-(3pyrrolin-1-yl)-1cyclopentenylmethylene]-rhodanine, sodium salt

1-(2-Anilinomethylenecyclopentylidene)-3pyrrolinium perchlorate (3.39 g), 3-carboxymethylr- 20 hodanine (1.91 g), acetic anhydride (1.0 ml), and triethylamine (3.0 ml) are dissolved in 4-butyrolactone (15 ml) and heated at a gentle reflux for 5 minutes. A solution of sodium iodide (2.00 g) in acetonitrile (50 lected on a filter. After one recrystallization from N,Ndimethylacetamide/acetonitrile and another from water/acetonitrile, the yield is 0.31 g (9 percent), m.p.  $= 257^{\circ}-258^{\circ} \text{ C dec.}$ 

It is sometimes desirable to supersensitize the dyes 30 also be used in practicing my invention. employed in this invention. Preferred supersensitizers are the polynuclear aromatic compounds containing at least one sulfo group. The term "polynuclear aromatic" as used herein is intended to mean 2 or more benzene rings fused together (for example, as in naphthalene, pyrene, etc) or at least 2 benzene rings or aromatic rings directly joined together (for example, as in diphenyl, terphenyl, quaterphenyl, etc) or through an aliphatic linkage. Such sulfonated derivatives can conveniently be presented by the following general for- 40 mula: XIV. T-SO<sub>3</sub>M

wherein T represents a polynuclear aromatic group as defined above and M represents a hydrogen atom or a water-soluble cation salt group (e.g., sodium, potassium, ammonium, triethylammonium, triethanolammonium, pyridinium, etc). Among the most useful of the sulfonated derivatives embraced by Formula XIV above are the compounds represented by the following general formula:

wherein T<sub>1</sub> represents a 1,3,5-triazin-6-ylamino group, <sup>6</sup> T<sub>2</sub> represents an aromatic group (i.e., benzene or substituted benzene) and M has the values given above.

Typical of the sulfonated derivatives of Formula XV above, wherein T<sub>1</sub> represents a 1,3,5-triazin-2-ylamino group (i.e., a 1,3,5-triazin-2-ylamino group) are the compounds selected from those represented by the following general formula:

wherein M has the values given above and R<sub>20</sub>, R<sub>21</sub>, R<sub>22</sub>, R<sub>23</sub> each represents a hydrogen atom or a substituent group, such as hydroxyl, aryloxyl (e.g., phenoxyl, otoloxyl, p-sulfophenoxyl, etc.), alkoxyl(e.g., methoxyl, ethoxyl, etc.), a halogen atom (e.g., chlorine, bromine, etc.), a heterocyclic radical (e.g., morpholinyl, piperidyl, etc.), an alkylthio group (e.g., methylthio, ethylthio, etc.), an arylthio group (e.g., phenylthio, tolylthio, etc.), a heterocyclylthio group (e.g., benzothiazylthio, etc.) an amino group, an alkylamino group (e.g., methylamino, ethylamino, propylamino, dimethylamino, diethylamino, dodecylamino, cyclohexylamino, β-hydroxyethylamino, di-β-hydroxyethylamino, β-sulfoethylamino, etc.), an arylamino group (e.g., anilino, o-, m- and p-anisylamino, o-, m- and pchloroanilino, o-, m- and p-toludino, o-, m-, and pcarboxyanilino, hydroxyanilino, sulfonaphthylamino, ml) is added and, after cooling, the crude dye is col- 25 o-, m- and p-aminoanilino, p-acetamidanilino, etc.),

Compounds of Formula XVI wherein R<sub>20</sub>, R<sub>21</sub>, R<sub>22</sub> and/or R<sub>23</sub> each represents a heterocyclylamino group (e.g., 2-benzothiazoleamino, 2-pyridylamino, etc.) can

Another group of sulfonated derivatives which are useful in practicing the invention are those represented by the following general formula:

wherein R<sub>24</sub> is an acylamido group (e.g., acetamido, 4-methoxy-3-sulfobenzamido, sulfobenzzmido, 2,4-diethoxy, benzamido, ethoxybenzamido, 4-methyl-2-methoxybenzamido, tolylamido, 2-naphthoylamino, naphthoylamino, 2-phenylbenzamido, dimethoxybenzamido, thienylbenzamido) or a sulfo group, R<sub>26</sub> represents an acylamido group (e.g., as defined by R24 above), or a sulfoaryl group (e.g., sulfophenyl, p'-sulfodiphenyl, 50 etc.) and R<sub>25</sub> represents a hydrogen atom or a sulfo group, said compound containing at least one sulfo group.

Compounds of Formula XVI which can advantageously be employed in practicing my invention have 55 been described in one or more of the following representative patents: U.S.:

50	2,171,427 2,472,475 2,595,030 2,660,578 2,945,762	Aug. 29, 1939 June 14, 1949 Apr. 29, 1952 Nov. 24, 1953 July 19, 1960
В	ritish:	

	595,065		Nov. 26, 1947
65	623,849	4.1	May 24, 1949
05	624,051		May 26, 1949
	624.052		May 26, 1949
	678.291		Sept. 3, 1952
	681,642		Oct. 29, 1952

Mar. 10, 1954

The products of Formula XVI have been previously employed in the textile field, and are sold under such tradenames as Leucophor B, Calcofluor White MR, Tinopal (SP, WR, BV277, 2B, GS, NG), Blancofor SC, Hiltamine (BSP, N, Sol., 6T6), and the like.

The dibenzothiophenedioxide compounds of Formula XVII have, in general, been previously described in the prior art. See, for example, U.S. Pat. Nos. 2,573,652; 2,580,234; and 2,563,493. Further examples of the preparation of such compounds are given in J. E. Jones, J. Spence, and J.A. VanAllan, U.S. Pat. No. 2,937,089, issued May 17, 1960. Still other examples of compounds represented by Formula XIV above which can be used in my invention have been previously described in B. H. Carroll, J. E. Jones, and J. Spence, U.S. Pat. No. 2,950,196, issued Aug. 23, 1960. (See, in particular, the compounds of Formulas II, III and IV of that patent).

Compounds selected from those of Formula XV above wherein T<sub>1</sub> represents a 2-benzotriazolyl group can be prepared according to methods previously described in the prior art. See, for example, U.S. Pat. to Zweidler et al. No. 2,713,057, dated July 12, 1955; Keller et al., U.S. Pat. No. 2,684,966, dated July 27, 1954; Zweidler et al., U.S. Pat. No. 2,784,197, dated Mar. 5, 1957; and Keller at al., U.S, Pat. No. 2,784,183, dated Mar. 5, 1956 A somewhat related group of compounds containing a 2-benzotriazolyl group which can be used in this invention have been previously described in U.S. Pat. No. 2,733,165. Such compounds are embraced by Formula IVa above.

Typical sulfonated derivatives embraced by Formulas XIV, XV and XVII an VIa above are (chemical formulas are given for various types to aid in identification):

1. a sulfonated triazolostilbene, e.g., of the type shown in U.S. Pat. No. 2,713,057.

4,4'-di(4'',6''-dihydroxy-2''-s-triazinylamino)stilbene-2,2'-disulfonic acid

3. 4,4'-bis[4-(3'-sulfoanilino)-6-amino-s-triazin-2- 50 ylamino]-stilbene

4. Tinopal-WR, a sulfonated triazinyl stilbene

5. Tinopal-2B, a sulfonated triazinyl stilbene

6. A sulfonated triazinyl stilbene, e.g., of the type shown in U.S. Pat. No. 2,595,030 or British Pat. 55 No. 595,065

7. 4,4'-bis[2-(4-sulfoanilino-2-\beta- hydroxyethylamino)-1,3,5-triazin-6-ylamino]stilbene-2,2'-disulfonic acid

8. 4,4'-bis(2,4-dihydroxy-1,3,5-triazin-6-ylamino)dibenzyl-2,2'-disulfonic acid

 4,4'-bis(2-β-hydroxyethylamino-4-anilino-1,3,5triazin-6-ylamino)-1,4-distynylbenzene-2,2'disulfonic acid

10. 5-methoxy-2-(4-styryl-3-sulfo)phenyl-1,2,3-65 benzotriazole sodium salt

11. Calcofluor White-MR, a sulfonated triazinyl stilbene

10 3,7-bis(2-phenylbenzamido)-2,8-disulfodibenzothio-phene-5,5-dioxide

13. 3,7-bis(2-thienylamide)-2,8disulfodibenzothiophene dioxide sodium salt

14. 3-[4-(4-methoxy-3-sulfobenzamidophenyl]-7-(4-methoxy-3-sulfobenzamide)dibenzothiophene dioxide sodium salt

15. chrysene-6-sulfonic acid sodium salt

16. pyrene-3-sulfonic acid sodium salt

17. Phenanthrene-3-sulfonic acid sodium salt

18. 2,3-dimethylnaphthalene-1-sulfonic acid sodium salt

 4-[4-phenoxy-6-(β-hydroxyethylamino)-striazin-2-ylamino]4'-[4-chloro-6-di(βhydroxyethyl)amino-s-traizin-2-ylamino]-stilbene-2,2'-disulfonic acid

20. 2,8-bis[4-(4-sulfoanilino)-6-hydroxy-s-triazin-2-ylamino]-carbazole

21. 4,4'-bis(4,6-di(β-hydroxyethylamino)-s-triazin-2-yl) benzidine-2,2'-disulfonic acid

22. 2-laurylamino-4,6-di(4-sulfoanilino)-s-triazine
23. 4,4'-bis 4-[4'-(N',4''-sulfobenzyl-N'-ethyl)aminoanilino]-6-hydroxy-s-triazin-2-ylamino

ethyl)aminoanilino]-6-hydroxy-s-triazin-2-ylamino stilbene-2,2'-disulfonic acid 24. 5-acetamido-2-(4-styryl-3-sulfo)phenyl-1,2,3-

benzotriazole sodium salt 25. 2,7-diacetamido-3,6-disulfodibenzothiophene-

5,5-dioxide sodium salt 26. 4-sulfo-o-terphenyl sodium salt (Lour. Organ. Chem., Vol. 14 (1949), pg. 163

27. pyrene-3-(4-methyl-3-sulfosytryl)ketone sodium salt

28. 3,7-bis(4-methyl-2-methoxybenzamido)-2,8-disulfodibenzothiophene-5,5-dioxide sodium salt

As can be seen above, many of the sulfonated derivatives are employed in the form of their water-soluble salts, such as alkali metal (e.g., sodium, potassium, etc.) salts, or ammonium or amine (e.g., triethylamine, triethanolamine, pyiridine, aniline, etc.) salts. By thus using these derivatives, they can be added to the emulsions in substantially neutral aqueous solutions without distrubing the pH of the emulsions.

In accordance with the practice of this invention, any reducing agent (i.e., a material capable of reducing silver halide) can be employed which supersensitizes photographic silver halide emulsions containing methine dyes of the type employed herein. Particularly good results are obtained with dihydroxy substituted reducing agents. Typical dihydroxy compounds which can be employed in the practice of this invention are selected from the group consisting of the benzenes, gammalactones, pyronimides, tetronimides, furans and pyrroles, which contain at least two hydroxyl groups.

Typical useful dihydroxy substituted compounds which can be utilized include hydroquinone, resorcinol, pyrocatechol, 3-methylpyrocatechol, toluhydroquinone, naphthalenediols, etc.; γ-lactones such as ascorbic acid, isoascorbic acid, etc.; 3-hydroxy tetroni-

mides; 3,4,5-trihydroxy-5,6-dihydro-pyronimides; and amino hexose reductones wherein the moiety comprising the subject reductones can be represented by the following formula

wherein R1 and R2 can be an alkyl radical, preferably having one to eight carbon atoms or together the neces- 10 Pat. No. 2,936,308. sary atoms to make a heterocyclic radical with the nitrogen atom, preferably having a 5 to 6 atom nucleus and including a second nitrogen atom or an oxygen atom such as morpholino, piperazino, pyrrolino, pyridino, pyrimidino, piperidino and the like.

Typical suitable tetronimides, pyronimides and amino hexose reductones are set out in Table B:

## TABLE B

5-Phenyl-3-hydroxy tetronimide

5-(4-Carboxyphenyl)-3-hydroxy tetronimide,

5-(3,4-Dimethoxyphenyl)-3-hydroxy tetronimide,

5-(n-Butyl)-3-hydroxy tetronimide

5-(2-Furyl)-3-hydroxy tetronimide

 $(5-\alpha$ -Furyl-3,4-dihydroxy-2-imino-2,5-dihydrofuran), and the like;

5,6-Diphenyl-3,4,5-trihydroxy-5,6-dihydro-pyronimide

5,6-Di-n-butyl-3,4,5-trihydroxy-5,6-dihydropyronimide,

5,6-Di-morpholino-3,4,5-trihydroxy-5,6-dihydropyronimide,

5,6-(2-Sulfophenyl)3,4,5-trihydroxy-5,6-dihydro-

pyronimide, and the like;

Dimethylamino hexose reductone

Di-n-butylamino hexose reductone

Di-n-hexylamino hexose reductone

Morpholino hexose reductone

Piperazino hexose reductone

Pyrrolino hexose reductone

Piperidino hexose reductone and the like.

The tetronimides an pyronimides such as mentioned above may be prepared by the methods described in British Pat. No. 782,304, Swiss Pat. No. 322,985, and in Helv. Chim. Acta, 39, 1780 (1956). The above, and still other 3-hydroxy tetronimides and 3,4,5-trihydroxy-5,6-dihydro-pyronimides that are suitable, are disclosed in Salminen, U.S. Pat. No. 3,330,655, issued July 11, 1967.

The amino hexose reductones of the invention are derived from sugars, especially D-glucose, although other six carbon or hexose reducing sugars such ad Dgalactose, D-mannose, D-fructose, L-sorbose or the like can be used. A typical method for preparing the subject reductones comprises heating in a reaction me-

dium substantially free of water a hexose reducing sugar and an aliphatic or cyclic secondary amine in the presence of an acidic reductone-forming catalytic agent such as phosphoric acid, boric acid, acetic acid, succinic acid or the like. The removal of three molecules of water results during the formation of the subject amino hexose reductones. The mentioned reductones and other related suitable reductones and methods for preparing such are described in Hodges, U.S.

Emulsions containing a methine dye of the type described above can be supersensitized with an azaindene, such as a triazaindene, a tetraazaindene or a pentaazaindene. Hydroxy and amino substituted azain-15 denes are especially useful. Representative useful azaindenes include those described in the following ref-

Allen et al. U.S. Pat. No. 2,735,769, Feb. 21, 1956 Allen et al. U.S. Pat. No. 2,743,181, Feb. 24, 1956

Tinker et al. U.S. Pat. No. 2,835,581, May 20, 1958 Reynolds U.S. Pat. No. 2,756,147, July 24, 1956 Carroll et al. U.S. Pat. No. 2,743,180, Apr. 24, 1956

Zeitschrift für Wiss, Phot. 47,2-28 (1952) Carroll et al. U.S. Pat. No. 2,716,062, Aug. 23, 1955

25 Allen et al. U.S. Pat. No. 2,772,164, Nov. 27, 1956 Allen et al. U.S. Pat. No. 2,713,541, July 16, 1955 Tinker U.S. Pat. No. 2,852,275, Sept. 16, 1958 Carroll U.S. Pat. No. 2,743,180, Apr. 24, 1956 Fry U.S. Pat. No. 2,566,658-9, Sept. 4, 1951

Heimbach et al. U.S. Pat. No. 2,444,605-7, July 6,

Hemibach et al. U.S. Pat. No. 2,449,225-6, Sept. 14,

Especially useful tetrazaindenes include those having the following formula:

in which R' is an alkyl group, e.g., methyl, ethyl, propyl, butyl, etc. Some particularly useful azaindenes are listed below:

4-hydroxy-2-β-hydroxy-ethyl-6-methyl-1,3,3a,7tetrazaindene

5-carbethoxy-4-hydroxy-1,3,3a,7-tetrazaindene 7-hydroxy-1,2,3,4,6-pentazaindene

2,4-dihydroxy-6-methyl-1,3a,7-triazaindene 4-hydroxy-2-γ-hydroxypropyl-6-methyl-1,3,3a,7tetrazaindene

4-hydroxy-2(4-pyridyl)-6-methyl-1,3,3a,7tetrazaindene

4-hydroxy-6-methyl-1,2,3,3a,7-pentazaindene 5-amino-2-(p-carboxyphenyl)-7-hydroxy-1,3,4,6-

pentazaindene 2,4-dihydroxy-6-methyl-1,3a,7-triazaindene

2,5-dimethyl-7-hydroxy-1,4,7a-triazaindene 5-amino-7-hydroxy-2-methyl-1,4,7a-triazaindene 5-carboxy-4-hydroxy-1,3,3a,7-tetrazaindene 1,2-bis(4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene-

5-yl(ethane 1,2,3,4-tetrakis(4-hydroxy-6-methyl-1,3,3a,7tetraazaindene-2-yl)butane

2-amino-5-carboxy-4-hydroxy-1,3,3a,7tetrazaindene

4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene

As noted above, azaindenes function as supersensitizer in emulsions containing various methine dyes. In some emulsions, the azaindene is advantageously used in combination with reducing agent, or preferably sulfonated organic compound supersensitizer, to produce emulsions having the best overall characteristics in terms of inherent emulsion speed, sensitized speed, low fog and storage stability.

According to the invention, one or more of the sulfo- 10 nated organic compounds or one or more of the azaindenes or one or more of the reducing agents, and one or more of the methine dyes, are added separately or together to light-sensitive photographic silver halide emulsions to supersensitize the emulsions. Particularly 15 good results are frequently obtained when both sulfonated organic compound and reducing agent are employed. In some emulsions, excellent results are obtained with the combination of an azaindene with a sulfonated organic compound supersensitizer. In other in- 20 stances, it is desirable to supersensitize emulsions with methine dye and sulfonated organic compound, reducing agent and azaindene. The dyes most effectively supersensitized with the compounds described above are the cyanines, particularly the carbocyanine, dicarbocy- 25 anine and tricarbocyanine dyes. The enamine tricarbocyanine dyes described herein, such as those of Formula II above, are particularly effective when used with supersensitizer.

The optimum concentration of methine dye and supersensitizer can be determined in a manner well known to those skilled in the art by measuring the sensitivity of test portions of the same emulsion, each portion containing a different concentration of dye and supersensitizer or mixture of supersensitizers. As a general guideline, good results are obtained with about 100 to 2,000 mg dye per mole of silver and about 25 to 2,000 mg and preferably 50 to 1,000 mg per mole of silver of the sulfonated organic supersensitizer.

The silver halide emulsions described herein can be unwashed or washed to remove soluble salts. In the latter case the soluble salts can be removed by chill-setting and leaching or the emulsion can be coagulation washed, e.g., by the procedures described in Hewitson et al U.S. Pat. No. 2,618,556; Yutzy et al. U.S. Pat. No. 2,614,928; Yackel U.S. Pat. No. 2,565,418; Hart et al. U.S. Pat. No. 3,241,969; and Waller et al. U.S. Pat. No. 2,489,341.

The noble metal and sulfur sensitizers can be added to the emulsion by conventional procedures, such as those described by Smith et al. in U.S. Pat. No. 2,448,0-60 issued Aug. 31, 1948. Generally, the sensitizers are added at the completion of Ostwald ripening and prior to final digestion.

The silver halide emulsions of this invention can contain speed increasing compounds such as polyalkylene glycols, cationic surface active agents and thioethers or combinations of these as described in Piper U.S. Pat. No. 2,886,437; Chechak U.S. Pat. No. 3,046,134; Carroll et al. U.S. Pat. No. 2,944,900; and Goffe U.S. Pat. No. 3,294,540.

Silver halide emulsions of this invention can be protected against the production of fog and can be stabilized against loss of sensitivity during keeping. Suitable antifoggants and stabilizers, which can be used alone or in combination, include the thiazolium salts described in Staud U.S. Pat. No. 2,131,038 and Allen U.S. Pat.

No. 2,694,716; the azaindenes described in Piper U.S. Pat. No. 2,886,437 and Heimbach U.S. Pat. No. 2,444,605; the mercury salts described in Allen U.S, Pat. No. 2,728,663; the urazoles described in Anderson U.S. Pat. No. 3,287,135; the sulfocatechols described in Kennard U.S. Pat. No. 3,236,652; the oximes described in Carroll et al. British Pat. No. 623,448; nitron; nitroindazoles; the mercaptotetrazoles described in Kendall etal. U.S. Pat. No. 2,403,927, Kennard et al. U.S. Pat. No. 3,266,897 and Luckey et al. U.S. Pat. No. 3,397,987; the polyvalent metal salts described in Jones U.S. Pat. No. 2,839,405; the thiuronium salts described in Herz U.S. Pat. No. 3,220,839; and the palladium, platinum and gold salts described in Trivelli U.S. Pat. No. 2,556,263 and Damschroder U.S. Pat. No. 2,597,915.

Photographic elements including emulsions prepared in accordance with this invention can contain incorporated developing agents such as hydroquinones, catechols, aminophenols, 3-pyrazolidones, ascorbic acid and its derivatives, reductones and phenylenediamines, or combinations of developing agents. The developing agents can be in a silver halide emulsion and/or in another suitable location in the photographic element. The developing agents can be added from suitable solvents or in the form of dispersions as described in Yackel U.S. Pat. No. 2,592,368 and Dunn et al. French Pat. No. 1,505,778.

Silver halide grains sensitized in accordance with the invention can be dispersed in colloids that can be hardened by various organic or inorganic hardeners, alone or in combination, such as the aldehydes, and blocked aldehydes, ketones, carboxylic and carbonic acid derivatives, sulfonate esters, sulfonyl halides and vinyl sulfones, active halogen compounds, epoxy compounds, aziridines, active olefins, isocyanates, carbodiimides, mixed function hardeners and polymeric hardeners such as oxidized polysaccharides, e.g., dialdehyde of starch, oxyguargum etc.

Photographic emulsions sensitized in accordance with this invention can contain various colloids alone or in combination as vehicles or binding agents. Suitable hydrophilic materials include both naturallyoccurring substances such as proteins, for example, gelatin, gelatin derivatives, cellulose derivatives, polysaccharides such as dextran, gum arabic and the like; and synthetic polymeric substances such as water soluble polyvinyl compounds, e.g., poly(vinyl-pyrrolidone) acrylamide polymers or other synthetic polymeric compounds such as dispersed vinyl compounds in latex form, and particularly those which increase the dimensional stability of the photographic materials. Suitable synthetic polymers include those described, for example, in U.S. Pat. No. 3,142,568 of Nottorf, issued July 28, 1964; 3,193,386 of White, issued July 6, 1965; 3,062,674 of Houck, Smith and Yudelson, issued Nov. 6, 1962; 3,220,844 of Houck, Smith and Yudelson, issued Nov. 30, 1965; Ream and Fowler 3,287,289, issued Nov. 22, 1966; and Dykstra U.S. Pat. No. 3,411,911; particularly effective are those waterinsoluble polymers of alkyl acrylates and methacrylates, acrylic acid, sulfoalkyl acrylates or methacrylates, those which have cross linking sites which facilitate hardening or curing and those having recurring sulfobetaine units as described in Canadian Pat. No. 774,054.

Emulsions supersensitized in accordance with this invention can be used in photographic elements which contain antistatic or conducting layers, such as layers that comprise soluble salts, e.g., chlorides, nitrates, etc., evaporated metal layes, ionic polymers such as 5 those described in Minsk U.S. Pat. No. 2,861,056 and 3,206,312 or insoluble inorganic salts such as those described in Trevoy U.S. Pat. No. 3,428,451.

Photographic emulsions containing the supersensitizing combinations of the invention can be coated on 10 may be coated simultaneously by the procedures dea wide variety of supports. Typical supports include cellulose nitrate film, cellulose ester film, poly(vinyl acetal) film, polystyrene film, poly(ethylene terephthalate) film, polycarbonate film and related films or resinous materials, as well as glass, paper, metal and the like. 15 et al. U.S. Pat. No. 2,716,059; silver salt diffusion trans-Typically, a flexible support is employed, especially a paper support, which can be partially acetylated or coated with baryta and/or an alpha-olefin polymer, particularly a polymer of an alpha-olefin containing two to 10 carbon atoms such as polyethylene polypropylene, 20 Rogers U.S. Pat. No. 3,087,817; 3,185,567; and ethylenebutene copolymers and the like.

Sensitized emulsions of the invention can contain plasticizers and lubricants such as polyalcohols, e.g., glycerin and diols of the type described in Milton U.S. Pat. No. 2,960,404; fatty acids or esters such as those 25 described in Robijns U.S. Pat. No. 2,588,765 and Duane U.S. Pat. No. 3,121,060; and silicone resins such as those described in DuPont British Pat. No. 955,061.

The photographic emulsions sensitized as described 30 herein can contain surfactants such as saponin, anionic compounds such as the alkyl aryl sulfonates described in Baldsiefen U.S. Pat. No. 2,600,831 and amphoteric compounds such as those described in Ben-Ezra U.S. Pat. No. 3,133,816.

Photographic elements containing emulsion layers sensitized as described herein can contain matting agents such as starch, titanium dioxide, zinc oxide, silica, polymeric beads including beads of the type described in Jelley et al. U.S. Pat. No. 2,992,101 and 40 Lynn U.S. Pat. No. 2,701,245.

Sensitized silver halide emulsions of the invention can be utilized in photographic elements which contain brightening agents including stilbene, triazine, oxazole and coumarin brightening agents. Water soluble brightening agents can be used such as those described in Albers et al. German Pat. No. 972,067 and McFall et al. U.S. Pat. No. 2,933,390 or dispersions of brighteners can be used such as those described in Jansen German Pat. No. 1,150,274 and Oetiker et al. U.S. Pat. No. 3,406,070.

Photographic elements containing emulsion layers sensitized by the invention can be used in photographic elements which contain light absorbing materials and filter dyes such as those described in Sawdey U.S. Pat. NO. 3,253,921; Gaspar U.S. Pat. No. 2,274,782; Carroll et al. U.S. Pat. No. 2,527,583 and Van Campen U.S. Pat. No. 2,956,879. If desired, the dyes can be mordanted, for example, as described in Milton and 60 Jones U.S. Pat. No. 3,282,699.

The sensitizing dyes (and other emulsion addenda) can be added to the photographic emulsions from water solutions or suitable organic solvent solutions, for example with the procedure described in Collins et 65 al. U.S. Pat. No. 2,912,343; Owens et al U.S. Pat. NO. 3,342,605; Audran U.S. Pat. No. 2,996,287 or Johnson et al. U.S. Pat. No. 3,425,835. The dyes can be dis-

solved separately or together, and the separate or combined solutions can be added to a silver halide emulsion, or a silver halide emulsion layer can be bathed in the solution of dye or dyes.

Photographic emulsions of this invention can be coated by various coating procedures including dip coating, air knife coating, curtain coating, or extrusion coating using hoppers of the type described in Beguin U.S. Pat. No. 2,681,294. If desired, two or more layers scribed in Russell U.S. Pat. No. 2,761,791 and Wynn British Pat. No. 837,095.

Emulsions sensitized as described herein are useful in colloid transfer processes such as described in Yackel fer processes such as described in Rott U.S. Pat. No. 2,352,014, Land U.S. Pat. No. 2,543,181, Yackel U.S. Pat. No. 3,020,155 and Land U.S. Pat. No. 2,861,885; color image transfer processes such as described in 2,983,606; Weyerts U.S. Pat. No. 3,253,915, Whitmore et al. U.S. Pat. No. 3,227,550; 3,227,551 and 3,227,552; and Land U.S. Pat. No. 3,415,644; 3,415,645; 3,415,646; and imbibition transfer processes as described in Minsk U.S. Pat. No. 2,882,156.

Silver halide emulsions containing the sensitizer combinations of this invention can be used in elements designed for color photography, for example, elements containing color-forming couplers such as those described in Frolich et al. U.S. Pat. NO. 2,376,679; Vittum et al. U.S. Pat. No. 2,322,027; Fierke et al. U.S. Pat. No. 2,801,171; Godowsky U.S. Pat. No. 2,698,794; Barr et al. U.S. Pat. No. 3,227,554 and Graham U.S. Pat. No. 3,046,129; or elements to be developed in solutions containing color-forming couplers such as those described in Mannes and Godowsky U.S. Pat. No. 2,252,718; Carrol et al. U.S. Pat. No. 2,592,243 and Schwan U.S. Pat. No. 2,950,970. Exposed photographic emulsions of this invention can be processed by various methods including processing in alkaline solutions containing conventional developing agents such as hydroquinones, catechols, aminophenols, 3-pyrazolidones, phenylenediamines, ascorbic acid derivatives, hydroxylamines, hydrazines and the like; web processing such as described in Tregillus et al. U.S. Pat. No. 3,179,517; stabilization processing as described in Yackel et al. "Stabilization Processing of Films and Papers," PSA Journal, Vol. 16B, Aug. 1950; monobath processing as described in Levy "Combined Development and Fixation of Photographic Images with Monobaths, " Phot. Sci. and Eng., Vol. 2, No. 3, October, 1958, and Barnes et al. U.S. Pat. No. 3,392,019. If desired, the photographic emulsions of this invention can be processed in hardening developers such as those described in Allen et al U.S. Pat. No. 3,232,761; in roller transport processors such as those described in Russell U.S. Pat. No. 3,025,779; or by surface application processing as described in Example 3 of Kitze U.S. Pat. No. 3,418,132.

The silver halide emulsions sensitized by this invention can be used for making lithographic printing plates such as by the colloid transfer of undeveloped and unhardened areas of an exposed and developed emulsion to a suitable support as described in Clark et al U.S. Pat. No. 2,763,553; to provide a relief image as described in Woodward U.S. Pat. No. 3,402,045 or Spencer U.S. Pat. No. 3,053,658; to prepare a relief printing

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plate as described in Baxter at al. U.S. Pat. No. 3,271,150.

The following examples are included for a further understanding of the invention.

## **EXAMPLES 1-8**

A set of examples are prepared with four variables in order to illustrate optimum conditions of noble metal and sulfur sensitization of a very fine grain gelatino silver iodobromide (2.5 mole percent iodide) Lippmann 10 emulsion of 0.05 µm grain size. The four variables are (1) level of noble metal sensitization, (2) level of sulfur sensitization, (3) length of time of the chemical sensitization at 65° C, and (4) the level of Dye A with which the emulsion was spectrally sensitized before coating 15 (see structure and name below). Each emulsion is exposed for 10 seconds to a tungsten 500W light source in an Eastman 1B Sensitometer and developed for 4 minutes in Kodak D-19 developer. The coatings are made at approximately 250 mg silver and 600 mg gela-20 tin per square foot on a cellulose acetate support. The results are shown in Table I below.

TABLE I

Example	Noble metal sensitizer (added as KAuCl <sub>4</sub> ), mg./per mole Ag	Sulfur sensitizer (added as Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ), mg./per mole Ag	Time of chemical sensitiza- tion at 65° C. (min.)	Dye A, mg./per mole Ag	Rela- tive clear speed	Fog	30
1	25 25 150 75 75 75 25	6. 5 6. 5 6. 5 2. 6 2. 6 16 6. 5	20' 20' 20' 20' 40' 10' 10' 20'	0 0 1, 450 1, 450 850 850 850 500	7. 8 0. 8 100. 0 363. 0 324. 0 259. 0 126. 0 85. 0	. 04 . 04 . 14 . 08 . 08 . 04	35

Example 1 shows the sensitivity of the primitive emulsion without chemical or spectral sensitization. Example 2 shows a marked decrease in speed upon gold and sulfur sensitization at levels in a range customarily used in the art. Upon spectral sensitization (Exam- 45 ple 3), a notable speed increase is observed. In Example 4 a substantially higher level of gold sensitization compared with Example 3 gives a relative speed increase from 100 to 363, accompanied by a small increase in fog. An intermediate but still high level of 50 gold sensitization is indicated in Examples 5 and 6 with lower levels of sulfur sensitization and dye. The relative speeds of these emulsions are high but not as high as in Example 4. Example 7 shows that an increase in sulfur sensitization actually causes a decrease in speed when 55 compared to Example 6. The higher the gold level, the greater the speed. The speed generally varies inversely with the sulfur and the dye levels. Example 8 compared with Example 3 shows little change in speed when a lower level of dye was used. However, the speed drops 60 substantially when the dye is omitted.

Dye A — Anhydro-3,9-diethyl-5,5'-dimethoxy-3'-(3-sulfopropyl)thiacarbocyanine hydroxide, the red sensitizer used in the examples above.

#### **EXAMPLE 9**

A series of gelatino silver iodobonomide Lippmann emulsions with varying iodide content from 0 to 18.8 mole percent is prepared. The grain size decreases as the iodide content increases. The emulsions are treated in three ways (A) given no further chemical sensitization, (B) chemically sensitized with 176 mg. sodium thiosulfate (23 mg. sulfur) plus 88 mg. potassium tetrachlorate (42 mg. gold) in the range 0 to 10 minutes at 65° C, and (C) chemically sensitized with 30 mg. sodium thiosulfate (3.9 mg. sulfur) plus 300 mg. potassium tetrachloraurate (144 mg. gold) in the range 0 to 10 minutes at 65° C. (Little change is noted within the 0 to 10 minutes time range.) All are coated with 300 mg. of Dye B per mole of silver. The results of photographic tests (conducted as in Examples 1-8) are given in Table II. The above concentrations are given in mg. per mole of silver.

Dye B — 3-Ethyl-5-[2-(3-pyrrolin-1-yl)-1-cyclopentenylmethylene]rhodanine.

### TABLE II

Emulsion		Average Grain Size	Relative Speed   Sensitization Me	al	
	Mole % I	(μm)	Α	В	C
	0	0.052	14	71	178
	4.7	0.043	16	23	170
ī	9.4	0.040	12	17	126
•	18.8	0.034		13	102
	*The relative	speeds are based	on the same scale as	Table I.	

The data show that the speed effects of the high gold sensitization C persist throughout a wide range of iodide content of the silver iodobromide emulsion. Much smaller speed gains are obtained from the high sulfur and lower gold sensitization (Treatment B). Although some speed loss is noted in going to higher iodide conent, the bulk of the effect is attributable to the decreasing grain size of the emulsion. Results generally similar to those in Table II are obtained when the noble metal sensitizer is an equivalent amount of gold, platinum or palladium added, e.g., in the form of potassium iodoaurate, auric trichloride, potassium aurithiocyanate, a compound of the formula:

ammonium chloropalladate, sodium chloroplatinate, ammonium chlororuthenate or ammonium chloroiridate. Also, generally similar results to those in Table II are obtained when the sulfur sensitizer is added in an equivalent amount of a sulfur sensitizer other than so- 5 dium thiosulfate, such as thiourea, thiosinamine. Likewise, results generally similar to those in Table II are obtained when the various methine dyes referred to herein are substituted for dye B.

A series of Lippman gelatin silver bromoiodide (2.5 10 mole percent of the halide being iodide) emulsions are prepared and coated on a cellulose acetate support at a concentration of 250 mg. silver per square foot and 1041 mg. gelatin per square foot. The emulsions are chemically sensitized with potassium tetrachloroaurate 15 and sodium thiosulfate, with 10 minute digestion at 65° C after addition of the chemical sensitizers. Various dyes, identified in Table T below, are added to the emulsions, which have the grain size and contain the concentration of chemical sensitizer given in the fol- 20 Silver halide grain size 0.09; 200 mg. potassium tetralowing tables. Supersensitizer "A" is 4,4'-bis[4,6-bis-ochloroanilino-s-triazin-2-yl amino]-2,2'-stilbenedisulfonic acid, sodium salt in amounts of 1,000 mg. per mole of silver and Supersensitizer B (ascorbic acid) in amounts of 500 mg. per mole of silver are added as is 25 described in the tables below. Each emulsion is exposed and developed as described in Examples 1-9 above, except that an exposure is made through Kodak Wratten Filters 35 and 2B to record the blue (365 line) 30 exposure.

#### **TABLE III**

Silver halide grain size 0.09; 300 mg. potassium tetrachloroaurate per mole of silver (about 150 mg. gold per mole of silver) and 30 mg. sodium thiosulfate (about 4 35 mg. sulfur per mole of silver):

	Sensiti-		
Mg. dye Super- Relative			
per mole sensi- blue	zation		
Dye of silver tizer speed	Fogmaximum		Davis
Con-			Dye
	0.07 —	40	Con-
	0.08 535	40	trol
	0.06 495		32
3 818 A 182	0.16 525		37
4 847 — 55	0.06 495		38
	0.06 490		39
5 - 510 - 200	0.00 490		Con-
Con-	0.00	1	trol
	0.08 —	45	32
600 — 200	0.08 540	43	32
	0.10 540		
7 810 A 174	0.09 540	- 11	40
7 810 A 174 6	0.08 565		40
8 562 — 148	0.08 565		121
9 548 105	0.11 550		
10 444 — 174	0.08 535		5.7
	0.06	50	Dye No.
	0.08 525		1
12 603 A 200 13 541 A 129	0.09 525		
			•
	0.08 570		2
	0.08 540		
1 125			
	0.12 Pan		3
17 125		55	
Con-			
trol — — 6.2	0.08		4
	0.07 540		
	0.08 525		
6 343 A+B 117	0.08 535		5
	0.06 525		-
	0.09 545	60	6
	0.07 535	00	U,
			7
	0.06 535		1
Con-			
	0.06 —		2
	0.06 540		8
	0.07 515		
22 820 — 58	0.08 525	65	
23 480 A 43 (	0.08 525		9
	0.08 525		
9 411 A 110 C	0.10 545		10
9 411 A 110 C 25 246 A 71 C	0.06 530		
23 240 71 /1	330		

		34			
10	296	_	245	0.08	535
26	437	Α	35	0.08	
Con-					
trol	-	<del></del>	2.2	0.02	<u> </u>
17	300		93	0.12	715
17	300	A+B	162	0.11	715
16	300	A+B	170	0.12	640
27	300	A+B	155	0.22	720
28	287	A+B	170	0.20	720
29	333	A+B	162	0.14	710
30	318	A+B	170	0.20	710
31	265	A+B	170	0.24	700
32	189	_	200	0.08	565
Con-					
trol	_		1.4	0.08	_
17	300	A+B	170	0.14	720
Con-					
trol			· <u>-</u>	0.06	
. 33	300	A ·	132	0.06	690
34	300	Α	170	0.06	640
- 17	300	Α .	144	0.10	715
35	291	Α	170	0.08	700
36	300		93	0.18	720
16	200		263	0.10	635

TABLE IV

chloroaurate per mole of silver (about 100 mg. gold per mole of silver) and 20 mg. sodium thiosulfate per mole of silver (about 2.6 mg. sulfur per mole of silver):

Dye	Mg. dye per mole of silver	Super- sensi- tizer	Relative blue speed	Fogma	Sensiti zation ximum
Con- trol		<u> </u>	4.0	0.06	
17	300	A+B	174	0.08	715
32	500	_	200	0.06	560
		TABLE	E V		4.5

Silver halide grain size 0.05 micron; 320 mg. potassium tetrachloroaurate per mole of silver (about 160 mg. gold per mole of silver) and 32 mg. sodium thiosulfate per mole of silver (about 4 mg. sulfur per mole of sil-

	Dye	Mg. dye per mole of silver	Super- sensi- sensitizer	Relative blue speed	Fogma	Sensiti- zation cimum
40	Con- trol			1.3	0.06	
	32	574		200	0.09	560
	37	558	_	78	0.09	565
	38	629		86	80.0	·
	39	1926		37	0.07	545
	Con-		in the sec		0.06	
45	trol 32	574		1.4 200	0.06 0.10	555
43	32	765	_	200	0.10	560
	40	671		209	0.10	550
	40	895	<u> </u>	200	0.12	550
	100					

1 1 1	-	· —	1.4	0.00
	574		200	0.10
	765		209	0.12
	671		209	0.10
	895	医基直性	200	0.12
	093		200	0.12
		TABLE	Т	
			Ī. 1 9.	
Dye 1			10 A A	
3-Ally	yl-5-[5,5-	dimethyl-3-(	3-pyrrolin-l	l-yl)-2-
cvc	lohexeny	lidene Jrhoda	anine	
		ro-1,3-dieth		
		olinylidene)e		-ethyl-
		uric acid	,	
		ethyl-2-benze	othiazolinyli	idene)-
eth	vlidene l-	2-(2-thiazoly	l)imino-4-	
imi	dazolidin	one	1713111110 1	
		ninoethyl)-5	1/3 athul 2	
1-(2-	rovereli	nylidene)eth	ulidonal 2 r	honul
		uric acid	Augene 1-2-f	menyi-
3,0,3	,8-DI-(U	imethylene)t	nazonnocai	r <del>-</del>
2 E4	yanıne p	erchlorate	.15 1 2	
3-Eth	yı-2-[4-(	3-pyrrolin-1-	yı)-1,3-	
pen	itadienyi	]benzothiazo	num perchi	orate
		,3'-diethyl-3		
		)-ethyl]benzi	midazolo-	4 1
		anine iodide		
		ethyl-5,5'-	4	200
	(trifluoro			
ben	ızimidazo	olocarbocyan	ine iodide	
2-[4-(	1-Piperio	dyl)- $\Delta^{1.3}$ -buta	idienyl]-β-	
nap	hthothia	zole ethiodid	le	
3-Eth	yl-5(3-m	ethyl-2-thiaz	olinylidene-	
	•			

ethylidene)-1-phenyl-2-thiohydantoin

35

 $I-[4-(4-morpholyl)-\Delta^{1,3}]$ 11 butadienyl]benzothiazole ethiodide 3-Ethyl-5-[(3-methyl-2-thiazolidinylidene)ethylidene]-1-(2-morpholinoethyl)-2-thiohydantoin 1-(2-Diethylaminoethyl)-5-](3-methyl-2-12 13 thiazolidinylidene)ethylidene]-3-phenyl-2thiohydantoin 14 3-Ethyl-5-{[3-(4-sulfobutyl-2-(3H)-benzoxazolylidene jethylidene rhodanine 3-Ethyl-5-[γ-(1-piperidyl)allylidene Jrhoda-15 nine 3-Ethyl-2 16 {2-[2,3,4,4a,5,6-hexahydro-7-(1pyrrolidinyl)-1-naphthyl]vinyl} {benzoxazolium 2,3,4,4a.5,6 3,3'-Diethyl-6,6'-dimethoxythiadicarbocya-17 nine p-toluenesulfonate
-Ethyl-2-[4-(1,2,5,6-tetrahydro-1-pyridyl)3,4-trimethylene-1,3-butadienyl]benzox-18 azolium perchlorate
2-[6-Ethoxycarbonyl-3-(1-pyrrolidinyl)-2cyclohexenylidene]methyl-3-ethylbenzothiazolium perchlorate 2,3'-Bis(3,3-diethoxypropyl)-9-ethyl-5,5'-diphenyloxacarbocyanine bromide 20 2,2'-Diethyloxacarbocyanine iodide 2,2'-Diethyl-8-methyloxacarbocyanine iodide 22 23 4,4'-Dichloro-2,2',8-triethyloxacarbocyanine 3,3'-Diethyl-4,4-dimethyl-4',5'-benzox 24 azolinothiacarbocyanine fluoborate
3-Ethyl-5[(3-ethyl-2-oxazolidinylidene)-25 ethylidene | rhodanine 4-[(-1-Ethyl-2(1)-β-naphthothiazolylidene)isopropylidene]-3-26 methyl-1-(p-sulfophenyl)-5-pyrazolone 3,3'-Diethyl-10,12-ethylene-11-(4-phenyl-1-piperazinyl(oxatricarbocyanine perchlorate 3,3'-Diethyl-10,12-ethylene-11-(1,2,3,4-27 28 tetrahydro-2-isoquinolyl)oxatricarbocyanine perchlorate (3,3'-Diethyl-10,12-ethylene-11-[4-(3-29 phenylpropyl)piperidiono]thiatricarbocya-nine perchlorate -Diethyl-10,12-ethylene-11-[4-(3-phenyl-30 propyl)piperidino]oxatricarbocyanine perchlorate 3,3'-Diethyl-10,12-ethylene-11-(1,2,5,6-31 tetrahydro-1-pyridyl)oxatricarbocyanine perchlorate 3-Ethyl-5-[2-(3-pyrroline-1-yl)-1-32 cyclopentenylmethylene]rhodanine 3-Ethyl-5-[1-indolinyl)-5,5-dimethyl-2-33 cyclohexen-1-ylidene lethylidene rhodanine Anhydro-3-methyl-9-(2-pyrrolyl)-3'-(3-sulfopropyl)-4,5;4',5'-dibenzothiacarbocyanine hydroxide 34 '-Dietyl-7,7'-dimethoxythiadicarbocya-35 nine iodide 2-[(1-Carboxymethyl-4-oxo-3-phenyl-2 36 thioxo-5-imidazolidenylidene)ethylidene]-3-ethyl-1-phenyl-5-[(1,3,3-trimethyl-2-indolinylidene)ethylidene]-4imidazolidinone 5-[2-(1-Azetidinyl)-1-cyclopentenylme-37 5-[2-(1-Azeumy))-1-tyclopeneryme-thylene]3-ethylrhodanine
3-Ethyl-5-[(3-ethyl-2(3)-benzox-azolyidene)isopropylidene rhodanine
Anhydro-1-allyl-5-chloro-3'-ethyl-5'-methoxy-3-(3-sulfopropyl)benzimidazolo-38 39 oxacarbocyanine hydroxide
3-Carboxymethyl-5-[2-(3-pyrrolin-1-yl)-1-cyclopentenylmethylene]rhodanine, 40

Silver halide emulsions sensitized as described herein are particularly useful in microelectronic manufacturing, e.g., solid state circuit production, and in the production of holograms. These materials are described, for example, in Kodak Data Book P-9, Kodak Films and Plates for Science and Industry, published by the Eastman Kodak Co., 1967. Emulsions employed for such purposes advantageously contain a high concentration of at least one removable and substantially photographically inert light absorbing dye, as described in Stevens British Pat. No. 1,139,062. Since these materials are generally exposed to a mercury vapor source which emits in the blue region of the spectrum at 405

nm and 436 nm and in the green region at 547 nm, it is desirable that the sliver halide exhibit high sensitivity to all three line exposures. The use of absorbing dyes to reduce image spread and produce images of exceptionally high sharpness reduces the speed and contrast of these elements as described in Kodak British Pat. No. 1,139,062. It is, therefore, desirable to increase either or both blue and green speeds. The combination of a benzothiazolinylidene-thiooxazolidinedione blue 10 sensitizer with the oxathiazolocarbocyanine green sensitizer described in Stevens British Pat. No. 1,139,062 gives increased blue sensitivity with little or no change in green sensitivity. An increased concentration of the green sensitizer (above that which normally causes de-15 sensitization) gives an increase in green sensitivity without a substantial loss of contrast.

A particularly useful sensitizer is 3-ethyl-5-(3-ethyl-2-benzothiazolinylidene)-2-thio-2,4-oxazolidine-dione, which can be used effectively at concentrations of about 600 to 800 mg. per mole of silver. An effective green sensitizer is 3,3'-diethyl-4'-methyloxathiazolocarbocyanine iodide, which can be used effectively at 400, and preferably at 800 mg. per mole of silver. The combination of such sensitizers provides good blue and green speeds when the emulsion is exposed to a mercury vapor illuminant. Also highly useful is the dye 3-ethyl-5-[2-(3-pyrrolin-1-yl)-1-cyclopentenylmethylene]rhodanine

 $H_2$   $H_2$  O O

which gives high contrast and a substantial speed increase on exposure to both blue and green radiation when employed in emulsions sensitized in accordance with the invention.

Good results are also obtained with cyanine, merocyanine or hemicyanine dyes having a tertiary aminoalkyl group substituted on a heterocyclic nitrogen atom of 6-chloro-3,3'-diethyl-1-(2such as morpholinoethyl)benzimidazolooxacarbocyanine dide. Other useful dyes and dye combinations include anhydro-9-ethyl-3,3'-di(3-sulfopropyl)-4,5;4',5'dibenzothiacarbocyanine hydroxide, sodium salt; anhydro-3-ethyl-9-methyl-3'-(3-sulfobutyl)thiacarbocyanine hydroxide; anhydro-1'-ethyl-3-(3-sulfobutyl)thia-3-ethyl-5-(3-ethyl-2-2'-cyanine hydroxide; benzothiazolinylidene)-2-thio-2,4-oxazolidinedione; 3,3'-diethyl-4'-methyloxathiazolocarbocyanine iodide; anhydro-3,9-diethyl-5,5'-dimethoxy-3'-(3-sulfopropyl)-thiacarbocyanine hydroxide; or, anhydro-9ethyl-5,5'-dimethoxy-3,3'-bis(3-sulfopropyl)thiacarbocyanine hydroxide, sodium salt.

The following dyes provide highly useful results: 3-ethyl-2-[4,6-neopentylene-6-(4-methyl-1-piperazinyl)-1,3,5-hexatrienyl]benzothiazolium iodide, 3-ethyl-2-[6-(4-ethoxycarbonyl-1-piperazinyl)-4,6-neopentylene-1,3,5-hexatrienyl]-benzothiazolium iodide, and 3-ethyl-2-[6-(4-ethoxycarbonyl-1-piperazinyl)-4,6-neopentylene-1,3,5-hexatrienyl]ben-

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zoxazolium iodide. These dyes can be used alone, or in combination with other dyes, such as 3,3'-diethyl-6,6'-dimethoxythiadi carbocyanine p-toluenesulfonate. These dyes, whether used alone or in combination with other dyes, can be supersensitized, e.g., with a polynuclear aromatic compound containing at least one sulfo group (such as 4,4'-bis[4,6-bis-o-chloroanilino-striazin-2-yl amino]-2,2'-stilbenedisulfonic acid, sodium salt), and/or a reducing agent (such as ascorbic acid).

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 photographic silver halide emulsion comprising light-sensitive silver halide grains having an average grain size up to about 0.2 micron; said silver halide grains being sensitized with the combination of a gold sensitizer, at a concentration of about 50 to 200 milligrams 20

sitizer, at a concentration of about 50 to 200 milligrams gold per mole of silver, and a sulfur sensitizer at a weight ratio of sulfur to gold of from 1:15 to 1:75; and, said silver halide being spectrally sensitized with at least one dye having one of the following formulas:

$$\begin{array}{c} R_{1}-N-(L=L)_{d-1}-C=L-(L=L)_{m-1}-C=(L-L=)_{n-1}=N-R_{2} \\ \times Q \\ \times Q$$

wherein Z, Z<sub>1</sub>, Z<sub>4</sub> and Z<sub>5</sub> each represents the nonmetallic atoms necessary to complete a heterocyclic nucleus containing from 5 to 6 atoms; each L represents a methine linkage; d, n, c, e and g each represents an integer of from one to two p and f each represents an integer of from one to three; m represents an integer of from one to five; R<sub>1</sub>, R<sub>2</sub>, R<sub>7</sub> and R<sub>8</sub> each represents an alkyl group or an aryl group; X and X2 each represents an acid anion; Q, Q1 and Q2 each represents the non-metallic atoms required to complete a nitrogencontaining heterocyclic nucleus containing from 5 to 6 atoms in the heterocyclic ring; D represents an engroup selected from a 2,3,4,4a,5,6-hexahydro-7-( 1-pyrrolidinyl)-1-naphthyl group; a 2.6.7.7a-tetrahydro-5-(1-pyrrolidinyl)-3-indenyl group, a 3-(1-pyrrolidinyl)-2-norbornen-2yl group; a 3-(1-pyrrolidinyl)-2-indenyl group or a group having 60 one of the following formulas:

15 and D¹ represents a group having the following formula:

25 2. A photographic silver halide emulsion as defined in claim 6 wherein the light-sensitive silver halide grains have an average grain size of from about 0.02 to about 0.09 micron.

3. A photographic silver halide emulsion comprising light-sensitive silver halide grains having an average grain size up to about 0.1 micron; said silver halide grains being sensitized with the combination of a gold sensitizer, at a concentration of about 50 to 200 milligrams gold per mole of silver, and a sulfur sensitizer at a weight ratio of sulfur to gold of from 1:15 to 1:75; and, said silver halide being spectrally sensitized with a methine dye having one of the following formulas:

wherein e and g each represents a positive integer of from one to two; f represents a positive integer of from one to three; L represents a methine linkage; R<sub>8</sub> represents an alkyl group or an aryl group; Z<sub>5</sub> represents the non-metallic atoms necessary to complete a heterocyclic nucleus containing from 5 to 6 atoms in the heterocyclic ring; Q<sub>1</sub> and Q<sub>2</sub> each represents the non-metallic atoms required to complete a heterocyclic nucleus containing from 5 to 6 atoms in the heterocyclic ring; X<sub>2</sub> represents an acid anion; D represents a group having one of the following formulas:

and, D<sup>1</sup> represents a group having the following formula:

4. A photographic gelatin silver halide emulsion in which the silver halide grains have an average grain size 25 of from about 0.02 to about 0.09 micron; said grains being sensitized with the combination of potassium tetrachloroaurate, at a concentration of about 125 to 175 mg. gold per mole of silver, together with sodium thiosulfate at a weight ratio of sulfur to gold of from 1:30 30 to 1:50; said silver halide being spectrally sensitized with 3-allyl-5-[5,5-dimethyl-3-(3-pyrrolin-1-yl)-2-cyclohexenylidene]rhodanine.

5. A photographic gelatin silver halide emulsion in which the silver halide grains have an average grain size of from about 0.02 to about 0.09 micron; said grains being sensitized with the combination of potassium tetrachloroaurate, at a concentration of about 125 to 175 mg. gold per mole of silver, together with sodium thiosulfate at a weight ratio of sulfur to gold of from 1:30 to 1:50; said silver halide being spectrally sensitized with 3,6;3,8-di-(trimethylene)thiazolino carbocyanine salt.

6. A photographic gelatin silver halide emulsion in which the silver halide grains have an average grain size of from about 0.02 to about 0.09 micron; said grains being sensitized with the combination of potassium tetrachloroaurate, at a concentation of about 125 to 175 mg. gold per mole of silver, together with sodium thiosulfate at a weight ratio of sulfur to gold of from 1:30 to 1:50; said silver halide being spectrally sensitized with 3-ethyl-5-[(3-methyl-2-thiazolidinylidene)ethylidene]-1-(2-morpholinoethyl)-2-thiohydantoin, said dye being supersensitized with 4,-4'-bis[4,6-bis-o-chloroanilino-s-triazin-2-yl)amino]-2,2'-stilbene-disulfonic acid, disodium salt.

7. A photographic gelatin silver halide emulsion in which the silver halide grains have an average grain size of from about 0.02 to about 0.09 micron; said grains being sensitized with the combination of potassium tetrachloroaurate, at a combination of about 125 to 175 mg. gold per mole of silver, together with sodium thiosulfate at a weight ratio of sulfur to gold of from 1:30 to 1:50; said silver halide being spectrally sensitized with 3-allyl-5-[5,5-dimethyl-3-(3-pyrrolin-1-yl)-2-cyclohexenylidene]rhodanine; 3-ethyl-2-{2-[2,3,4,4a,5,6-hexahydro-7-(1-pyrrolidinyl)-1-

naphthyl]vinyl} benzoxazolium salt; and, 3,3'-diethyl-6,6'-dimethoxythiadicarbocyanine salt, said dyes being supersensitized with 4,4'-bis[4,6-bis-o-chloroanilino-striazin-2-yl)amino]-2,2'-stilbenedisulfonic acid, disodium salt and ascorbic acid.

8. A photographic gelatin silver halide emulsion in which the silver halide grains have an average grain size of from about 0.02 to about 0.09 micron; said grains being sensitized with the combination of potassium tet10 rachloroaurate, at a concentration of about 125 to 175 mg. gold per mole of silver, together with sodium thiosulfate at a weight ratio of sulfur to gold of from 1:30 to 1:50; said silver halide being spectrally sensitized with 3-ethyl-5-[2-(3-pyrrolin-1-yl)-1-cyclopentenylme15 thylene | rhodanine.

9. A photographic gelatin silver halide emulsion in which the silver halide grains have an average grain size of from about 0.02 to about 0.09 micron; said grains being sensitized with the combination of potassium tetrachloroaurate, at a concentration of about 125 to 175 mg. gold per mole of silver, together with sodium thio sulfate at a weight ratio of sulfur to gold of from 1:30 to 1:50; said silver halide being spectrally sensitized with 3-carboxymethyl-5-[2-(3-pyrrolin-1-yl)-1-cyclopentenylmethylene]rhodanine, sodium salt.

10. A photographic gelatin silver halide emulsion in which the silver halide grains have an average grain size of from about 0.02 to about 0.09 l micron; said grains being sensitized with the combination of potassium tetrachloroaurate, at a concentration of about 125 to 175 mg. gold per mole of silver, together with sodium thiosulfate at a weight ratio of sulfur to gold of from 1:30 to 1:50; said silver halide being spectrally sensitized with 3-ethyl-2- {2-{2,3,4,4a%,'-hexahydro-7-(1-pyrrolidinyl)-1naphthyl]vinyl}benzoxazolium salt.

11. A photographic gelatin silver halide emulsion in which the silver halide grains have an average grain size of from about 0.02 to about 0.09 micron; said grains being sensitized with the combination of potassium tetrachloroaurate, at a concentration of about 125 to 175 mg. gold per mole of silver, together with sodium thiosulfate at a weight ratio of sulfur to gold of from 1:30 to 1:50; said silver halide being spectrally sensitized with 5,6-dichloro-1,3'-diethyl-3-[2-(1-pyrrolidinyl) ethyl]benzimidazolo-oxacarbocyanine salt.

12. A photographic gelatin silver halide emulsion in which the silver halide grains have an average grain size of from about 0.02 to about 0.09 micron; said grains being sensitized with the combination of potassium tetrachloroaurate, at a concentration of about 125 to 175 mg. gold per mole of silver, together with sodium thiosulfate at a weight ratio of sulfur to gold of from 1:30 to 1:50; said silver halide being spectrally sensitized with 3-ethyl-5-(3-methyl-2-thiazolinylidene-ethylidene)-1-phenyl-2-thiohydantoin.

13. A photographic gelatin silver halide emulsion in which the silver halide grains have an average grain size of from about 0.02 to about 0.09 micron; said grains being sensitized with the combination of potassium tetrachloroaurate, at a concentration of about 125 to 175 mg. gold per mole of silver, together with sodium thiosulfate at a weight ratio of sulfur to gold of from 1:30 to 1:50; said silver halide being spectrally sensitized with 3,3'-diethyl-6,6'-dimethoxythiadicarbocyanine salt.

14. A photographic gelatin silver halide emulsion in which the silver halide grains have an average grain size

of from about 0.02 to about 0.09 micron; said grains being sensitized with the combination of potassium tetrachloroaurate, at a concentration of a bout 125 to 175 mg. gold per mole of silver, together with sodium thiosulfate at a weight ratio of sulfur to gold of from 1:30 5 to 1:50, said silver halide being spectrally sensitized anhydro-3,9-diethyl-5,5'dimethoxy-3'-(3sulfopropyl)thiocarbocyanine hydroxide.

15. A photographic gelatin silver halide emulsion in which the silver halide grains have an average grain size 10 of from about 0.02 to about 0.09 micron; said grains being sensitized with the combination of potassium tetrachloroaurate, at a concentration of a bout 125 to 175 mg. gold per mole of silver, together with sodium thiosulfate at a weight ratio of sulfur to gold of from 1:30 15 to 1:50, said silver halide being spectrally sensitized with anhydro-9-ethyl-5,5'-dimethoxy-3,3'-bis(3-sulfopropyl)thiacarbocyanine hydroxide, sodium salt.

16. A photographic gelatin silver halide emulsion in which the silver halide grains have an average grain size 20 rachloroaurate, at a concentration of about 125 to 175 of from about 0.02 to about 0.09 micron; said grains being sensitized with the combination of potassium tetrachloroaurate, at a concentration of about 125 to 175 mg. gold per mole of silver, together with sodium thiosulfate at a weight ratio of sulfur to gold of from 1:30 25 to 1:50, said silver halide being spectrally sensitized with 6-chloro-3,3'-diethyl-1-(2-moropholinoethyl)benzimidazolooxacarbocyanine salt.

17. A photographic gelatin silver halide emulsion in which the silver halide grains have an average grain size 30 of from about 0.02 to about 0.09 micron; said grains being sensitized with the combination of potassium tetrachloroaurate, at a concentration of about 125 to 175 mg. gold per mole of silver, together with sodium thiosulfate at a weight ratio of sulfur to gold of from 1:30 35 said sulfur sensitizer is present at a ratio of sulfur to to 1:50, said silver halide being spectrally sensitized 3-ethyl-2-[4,6-neopentylene-6-(4-methyl-1-

piperazinyl)-1,3,5-hexatrienyl]benzothiazolium salt together with 3,3'-diethyl-6,6'-dimethoxythiadicarbocyanine salt.

18. A photographic gelatin silver halide emulsion in which the silver halide grains have an average grain size of from about 0.02 to about 0.09 micron; said grains being sensitized with the combination of potassium tetrachloroaurate, at a concentration of about 125 to 175 mg. gold per mole of silver, together with sodium thiosulfate at a weight ratio of sulfur to gold of from 1:30 to 1:50, said silver halide being spectrally sensitized 3-ethyl-2-[6-(4-ethoxycarbonyl-1-piperazinyl)-4,6-neopentylene-1,3,5-hexatrienyl]benxothiazolium salt together with 3,3'-diethyl-6,6'-dimethoxythiadicarbocvanine salt.

19. A photographic gelatin silver halide emulsion in which the silver halide grains have an average grain size of from about 0.02 to about 0.09 micron; said graisn being sensitized with the combination of potassium tetmg. gold per mole of silver, together with sodium thiosulfate at a weight ratio of sulfur to gold of from 1:30 to 1:50, said silver halide being spectrally sensitized 3-ethyl-2-[6-(4-ethoxycarbonyl-1-piperazinyl)-4,6-neopenthylene-1,3,5-eexatrienyl]benzoxazolium salt together with 3,3'-diethyl-6,6'-dimethoxythiadicarbocyanine salt.

20. In a light sensitive photographic silver halide emulsion comprising silver halide grains having a grain size up to about 0.2 micron, which grains are spectrally sensitized with a methine dye and chemically sensitized with a gold sensitizer and a sulfur sensitizer, the improvement wherein said gold sensitizer is present at a concentration of at least 50 mg. per mole of silver, and gold of from 1:15 to 1:75.

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