

[54] SPECTRALLY SENSITIZED SILVER
HALIDE PHOTOGRAPHIC EMULSION[75] Inventors: Keisuke Shiba; Akira Sato; Akira
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[51] Int. Cl..... G03c 1/14

[58] Field of Search..... 96/126, 140

[56] References Cited

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Zinn & Macpeak

[57] ABSTRACT

A silver halide photographic emulsion sensitized with the combination of (1) at least one dimethine merocyanine dye wherein the carbon atom at the 2-position of an oxazole nucleus bearing an alkyl group containing a sulfo or a carboxyl group on the nitrogen atom at the 3-position thereof and the carbon atom at the 5-position of a 2-thiohydantoin nucleus bearing a hydrogen atom or an alkyl group on the nitrogen atom at the 1- and 3-positions thereof are connected with each other through a dimethine chain, and (2) at least one of a J-band type carbocyanine dye wherein a sulfo group-containing alkyl group is attached to the nitrogen atom at the 3-position of a naphthothiazole nucleus, a naphthoselenazole nucleus, a benzothiazole nucleus or a benzoselenazole nucleus and the carbon atom at the 2-position is attached to mesoalkyl-substituted trimethine chain is disclosed.

17 Claims, 6 Drawing Figures

FIG 1

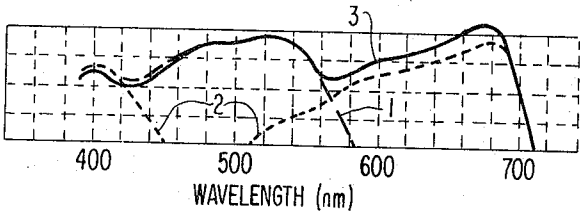


FIG 2

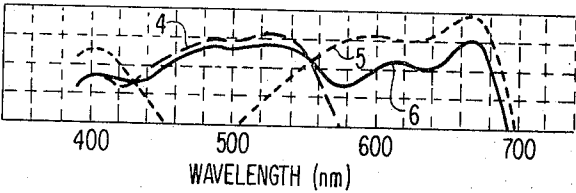


FIG 3

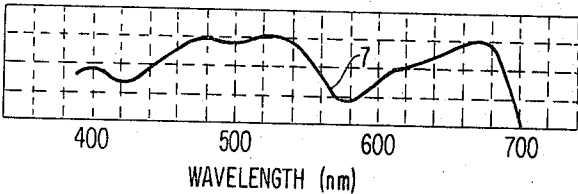


FIG 4

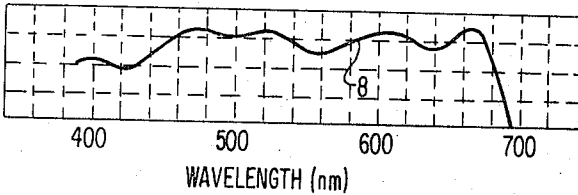


FIG 5

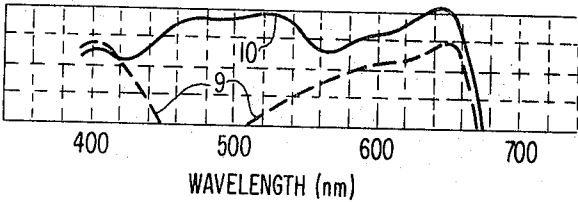
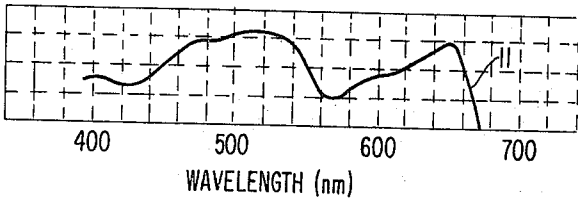


FIG 6



SPECTRALLY SENSITIZED SILVER HALIDE PHOTOGRAPHIC EMULSION

BACKGROUND OF THE INVENTION

1. FIELD OF THE INVENTION

The present invention relates to a panchromatically and spectrally sensitized silver halide photographic emulsion, and more particularly, it relates to a silver halide emulsion providing especially high red sensitivity with less stain and excellent contrast, wherein the synergistic effect caused by the combination of a special type of merocyanine dye and special type of red sensitive carbocyanine dye having a tendency to form J-band is utilized.

2. DESCRIPTION OF THE PRIOR ART

It has been known to use various types of merocyanine dyes for the spectral sensitization of a silver halide photographic emulsion. The spectrally sensitizing action obtained, especially in the merocyanine dyes, depends upon the properties of the emulsion used, such as the halogen composition, the crystal habit, the grain size, the pAg and the pH of the emulsion, and the manner of chemical sensitization, as well as the chemical structure of the sensitizing dyes and the physical properties thereof. Most of the merocyanine dyes in a single employment adsorb directly on the silver halide grains in the emulsion to function as a M-band type of spectral sensitizer. When used together with cyanine dyes, most of the merocyanine dyes tend to destroy the J-aggregate formed by the cyanine dyes, and hence they have a tendency to deteriorate the spectrally sensitizing action of the cyanine dyes.

It is extremely useful to use the cyanine dyes in the J-aggregate state for the sensitization of a silver halide photographic emulsion in the red wavelength region of from 590 to 690 nm. Especially, it is useful for providing an emulsion with high contrast. This is based on the fact that, generally speaking, the cyanine dyes having shorter light absorption wavelength in an alone state are chemically stable and, in a J-aggregation state, they then absorb light of longer wavelengths by several tens of nanometers in spite of the short methine chain. A J-aggregate can provide narrow light absorption and, in addition, can provide light absorption in the longer wavelength region than M-band by several tens of nanometers.

However, the J-aggregate formed by the cyanine dyes tend to be destroyed also by co-existing dyestuffs, chemical sensitizers, stabilizing agents, fog inhibitors, surface active agents, hydrophilic synthetic polymers, color couplers, development accelerators and inhibitors.

In most cases, panchromatic sensitization of a silver halide emulsion can be attained by two or more of the sensitizing dyes. In this case, it is extremely important to develop useful special combinations wherein the spectral sensitizations with the individual sensitizing dye can be enhanced by each other.

Incomplete removal of the sensitizing dyes used from a light-sensitive material during the step of development processing of the light-sensitive material will cause a staining of the resulting images. On the other hand, in order to provide a strong spectrally sensitizing action, the sensitizing dyes must be very strongly adsorbed on the silver halide grains. Generally speaking, in the case of the merocyanine dyes, the direction of

the adsorption property and the direction of the reduction in stain are opposite with each other.

An object of the invention is to improve the above-described defects.

That is, an object of the invention is to provide a panchromatically supersensitized light-sensitive material with excellent contrast for industrial recording.

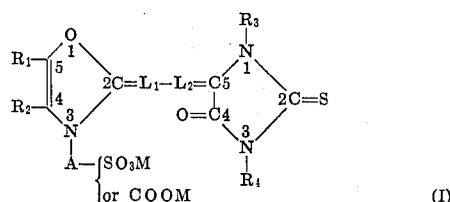
Another object of the invention is to provide a silver halide photographic emulsion having an especially high gamma and high red sensitivity.

A further object of the invention is to provide merocyanine dyes which act as supersensitizers for the panchromatically sensitizing carbocyanine dyes and to provide high ortho sensitivity with less stain.

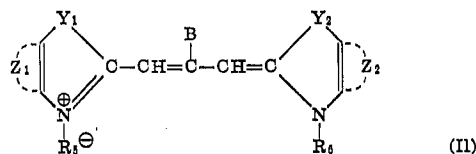
A still further object of the invention is to provide a silver halide photographic emulsion which provides images having less fog and excellent grain property.

SUMMARY OF THE INVENTION

It has now been found that the above-described objects of the invention can be accomplished as described hereinafter, whereby the above stated defects can be improved. That is, the objects of the invention have been attained by the combined use of at least one of the dimethine merocyanine dyes wherein the carbon atom at the 2-position of an oxazole nucleus bearing an alkyl group containing a sulfo or a carboxyl group on the nitrogen atom at the 3-position thereof and the carbon atom at the 5-position of a 2-thiohydantoin nucleus are connected with each other through a dimethine chain, preferably at least one of the dyes represented by the following general formula (I);



wherein R_1 and R_2 each represents a hydrogen atom, a lower alkyl group, an aryl group or R_1 and R_2 may be combined to form an aromatic ring of the benzene series or of the naphthalene series, R_3 and R_4 each represents a hydrogen atom, an alkyl group, L_1 and L_2 each represents a methine group, A represents a divalent aliphatic group, and M represents a cation, and at least one of the J-band forming carbocyanine dyes comprising two cyanine nuclei selected from the group consisting of a naphthothiazole, a naphthoselenazole, a benzothiazole and a benzoselenazole nucleus, the nitrogen atom at the 3-position of at least one nucleus being attached to a sulfo group and the carbon atom at the 2-position being attached to a mesoalkyl substituted trimethine chain, preferably at least one of the dyes represented by the following general formula (II);



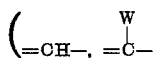
Wherein Y_1 and Y_2 each represents a sulfur atom or a selenium atom, B represents a lower alkyl group having 3 or less carbon atoms, Z_1 and Z_2 each represents the atoms necessary to complete an aromatic ring of the benzene series or of the naphthalene series, R_5 and R_6 each represents a lower alkyl group or a sulfo group containing alkyl group, and wherein at least one of R_5 and R_6 is a sulfo group containing alkyl group capable of forming a betaine structure, in a silver halide photographic emulsion.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1 to 6 are spectrograms comparatively shown in order to explain the invention in detail.

DETAILED DESCRIPTION OF THE INVENTION

As described above, in the above general formula (I), R_1 and R_2 represent hydrogen atoms, lower alkyl groups preferably having up to 4 carbon atoms (e.g., methyl, ethyl, etc.), aryl groups (e.g., phenyl, substituted phenyl wherein the substituent is a alkyl group, a sulfo group and the like, such as tolyl and sulfophenyl, etc.), or when taken together, R_1 and R_2 represent the atoms capable of forming an aromatic ring of the benzene series (e.g., a benzoxazole nucleus, substituted benzoxazole nucleus wherein the substituent is an alkyl group, a halogen atom, a hydroxyl group, an alkoxy group, an aryl group, an acetoxy group and the like, such as a 5-methylbenzoxazole nucleus, a 6-methylbenzoxazole nucleus, a 5-chlorobenzoxazole nucleus, a 5-hydroxybenzoxazole nucleus, a 5-methoxybenzoxazole nucleus, a 5-chloro-6-methylbenzoxazole nucleus, a 5-phenylbenzoxazole nucleus, and a 5-acetoxybenzoxazole nucleus, etc.) or an aromatic ring of the naphthalene series, (e.g., α -naphthoxazole nucleus, β , β -naphthoxazole nucleus, β -naphthaxazole nucleus, etc.), R_3 and R_4 represent hydrogen atoms, or alkyl group [(e.g., methyl, ethyl, 2-propenyl, hydroxyalkyl (e.g., hydroxyethyl), acetoxyalkyl (e.g., acetoxypropyl), aminoalkyl (e.g., aminoethyl, dimethylaminoethyl), carboxyalkyl (e.g., carboxyethyl), sulfoalkyl (e.g., 3-sulfopropyl, 3-sulfobutyl), aralkyl (e.g., benzyl), etc., the alkyl moiety thereof being preferably a lower alkyl group having from 1 to 4 carbon atoms], L_1 and L_2 represent methine groups



(wherein W represents, for example, an alkyl (e.g., methyl), hydroxyalkyl (e.g., hydroxypropyl), carboxyalkyl (e.g., carboxyethyl), aryl (e.g., carboxyphenyl), alkoxy (e.g., methoxy group), etc.), A represents a divalent aliphatic group (e.g., ethylene, propylene, butylene, isopropylene, propenylene, the groups described in *Zeitschrift fur wissenschaftliche Photographie*, vol. 63, pp.149 pp. 158 (1967), written by E.J. Poppe, etc.), M represents a cationic group capable of forming a sulfonate or a carboxylate (e.g., a sodium ion, an ammonium ion, a hydrogen ion, a thiouronium ion, etc.).

In the above-illustrated general formula (II), Y_1 and Y_2 represent sulfur or selenium atoms, B represents a lower alkyl group having 3 or less carbon atoms (e.g., methyl, ethyl, propyl, etc.), Z_1 and Z_2 represent the

atoms necessary to complete an aromatic ring of the benzene series (e.g., benzothiazole, substituted benzothiazole wherein the substituent is a halogen atom, an alkoxy group, an alkyl group and the like, such as 5-chlorobenzothiazole, 5,6-dichlorobenzothiazole, 5-methoxycarbonylbenzothiazole, 5-methoxybenzothiazole, 5-bromobenzothiazole, and 5-methylbenzothiazole, benzoselenazole, substituted benzoselenazole wherein the substituent is an alkyl group, an alkoxy group, a hydroxy group, an aryl group, and the like, such as 5-methylbenzoselenazole, 5-ethoxybenzoselenazole, 5-hydroxybenzoselenazole, 5-phenylbenzoselenazole nucleus, etc.) or an aromatic ring of the naphthalene series (e.g., naphthothiazole, naphthoselenazole nucleus, etc.), R_5 and R_6 represent an alkyl group (e.g., methyl, ethyl, propyl, propenyl, hydroxyalkyl (e.g., hydroxyethyl), amidoalkyl (e.g., amidoethyl), acetoxyalkyl (e.g., acetoxypropyl), carboxyalkyl (e.g., carboxyethyl, carboxypropyl group), etc., the alkyl moiety thereof being a lower alkyl group having preferably from 1 to 6 carbon atoms), or a sulfo group-containing alkyl group (e.g., a sulfoethyl, sulfo-propyl, 3-sulfobutyl, 4-sulfobutyl, 2-(3-sulfopropoxy)ethyl, 2-[(3-sulfopropoxy)ethoxy]ethyl, sulfatopropyl group, the groups described in *Zeitschrift fur wissenschaftliche Photographie* vol. 63, pp. 149 - 158 (1969), written by E. J. Poppe, etc.), at least one of R_5 and R_6 being a sulfo group-containing alkyl group which is capable of forming a betaine structure.

A first characteristic of the invention is due to the chemical structure of the merocyanine dyes used in the invention.

The chemical structure of the merocyanine dyes used in the invention is characterized by the oxothiohydantoin dimethine merocyanine, especially in the connection of the nitrogen atom in the oxazole nucleus to an alkyl group containing a sulfo group, and in the special combination of an oxazole nucleus and a thiohydantoin nucleus in one molecule.

Generally speaking, the oxothiohydantoin dimethine merocyanine dyes are disclosed in U.S. Pat. Nos. 2,493,748; 2,519,001; and 3,480,439; Japanese Patent Publication Nos. 18105/71; 18106/71; 18108/71; and 2606/68; Belgian Patent Nos. 648,068; 701,921; and 718,631; and French Patent No. 1,451,598.

The merocyanine dyes in accordance with the invention have the characteristics that, when used independently, they provide M-band type high sensitivity in the green wavelength region without forming fog, and that less stains are formed after development processing.

The merocyanine dyes described in U.S. Pat. No. 2,493,748 relate to merocyanine dyes having an acidic group in a keto nucleus, which is mainly a rhodanine nucleus or an oxazolidione nucleus, and there is no specific description of the presence of a thiohydantoin nucleus having sulfo group. Accordingly, the dyes described in the U.S. Pat. No. 2,493,748 are absolutely different from the dye of the invention.

The merocyanine dyes described in U.S. Pat. No. 2,519,001 relates to merocyanine dyes having a sulfoalkyl group or a carboxy-alkyl group at the cyanine nucleus thereof, but nothing is described therein with respect to the oxothiohydantoin dimethine merocyanine dyes in accordance with the invention and the effects of the invention.

In the merocyanine dyes of the invention, a sulfo group-containing alkyl group is attached to the nitro-

gen atom in a basic oxazole nucleus, and the dyes adsorb on the silver halide grains better than the merocyanine dyes described in U.S. Pat. No. 2,493,748, are much less adversely affected by the co-presence of other additives, and tend to provide high sensitivity. Furthermore, they change very little in sensitivity due to a variation in the substituents at the 1- and the 3-positions of a 2-thiohydantoin nucleus (e.g., methyl, propyl, phenyl, benzyl, etc.), and tend to provide high sensitivity with substituents having a small size such as a methyl, an ethyl group etc. and derivatives thereof. Of course, the merocyanine dyes in accordance with the invention have the advantage that they form less stains.

The object of the invention of French Patent No. 1,451,598 is to form J-band by introducing specific alkyl groups into the 1- and the 3-positions of a 2-thiohydantoin nucleus to utilize the J-band. In this connection, if an n-propyl group or an n-butyl group is attached to either the 1- or the 3-position of the 2-thiohydantoin nucleus, stains tend to increase, which is against the object of the present invention.

A second characteristic of the invention (which is a most important point of the invention) is that, when the merocyanine dyes and the carbocyanine dyes in accordance with the invention are used in combination, the gamma in the wavelength region sensitized with the carbocyanine dyes is markedly enhanced and a high sensitivity can be obtained without degrading the sensitivity in the wavelength region sensitized with the merocyanine dyes. It should be noted that the effect of the merocyanine dyes to raise the gamma in the red sensitive wavelength region caused by the cyanine dyes has not so far been known. A detailed description thereof will be given in the specific examples set forth hereinafter.

U.S. Pat. No. 2,430,558 discloses the fact that combination of the so-called "acid merocyanine dyes" containing a sulfo or a carboxyl group at a keto nucleus with the "basic trimethine cyanine dyes" produce supersensitization. However, the compounds described in the above patent specification, being merocyanine dyes or trimethine cyanine dyes, are absolutely different in chemical structure from the dyes in accordance with the invention, and, in addition, there is no specific description in the above patent specification of a merocyanine dye having a 2-thiohydantoin nucleus, much less of the effect of the enhancement of the sensitivity and the provision of contrast in the red supersensitized wavelength region, and a reduction in stains.

A third characteristic of the invention lie in the chemical structure of the carbocyanine dyes. The merocyanine dyes in accordance with the invention do not provide all the carbocyanine dyes with above-described useful effects, but provide only certain carbocyanine dyes of the invention with such effects.

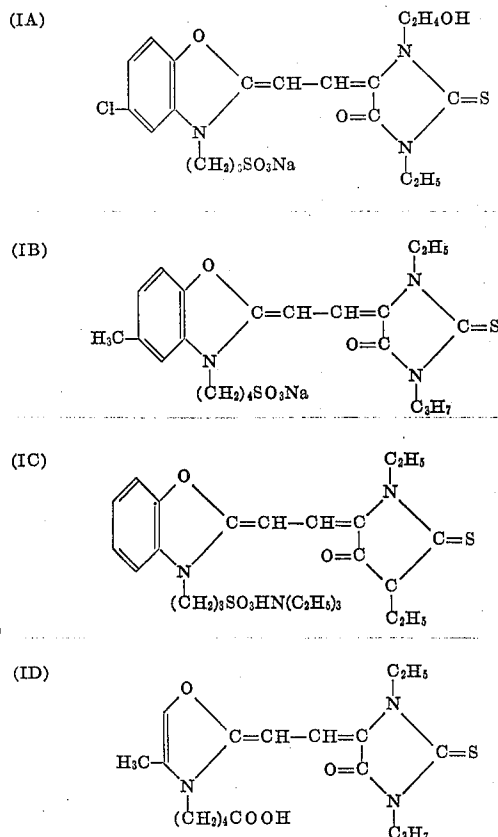
The merocyanine dyes of the invention do not act as supersensitizers of the trimethine cyanine dyes disclosed in U.S. Pat. No. 2,430,558, and, in many cases, on the contrary they degrade the red sensitivity, as described in the examples given hereinafter.

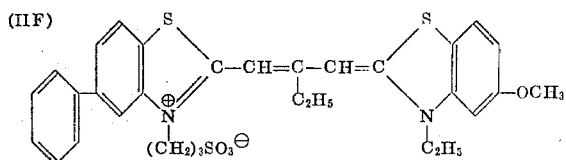
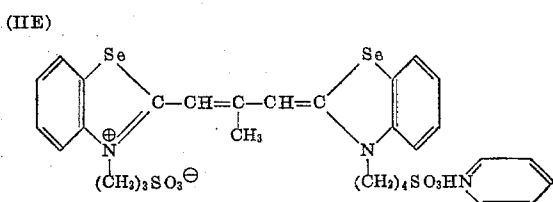
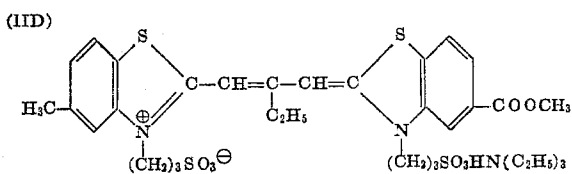
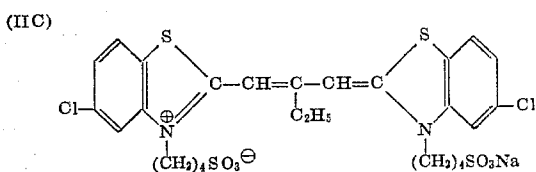
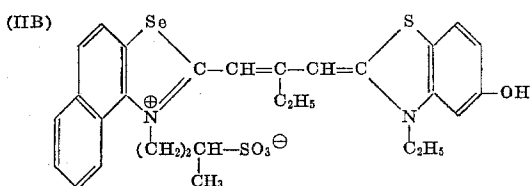
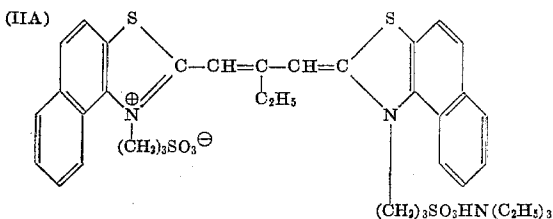
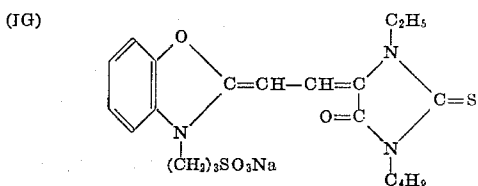
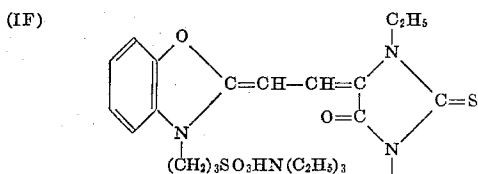
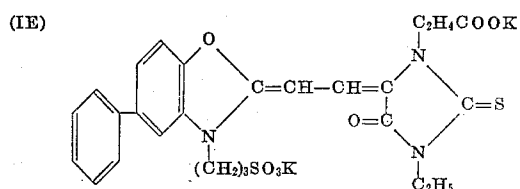
No description of the special effect produced by the combined use of the dyes in the present invention can be found in Japanese Patent Publication Nos. 2606/68; 18105/71; 18106/71; and 18108/71; Belgian Patent Nos. 701,921; 716,831; and 690,096; British Patent No. 1,112,036; and U.S. Pat. No. 3,480,439, either.

Suitable silver halide emulsions which can be used in the invention are mixed silver halide emulsions with any mixing ratio of chlorine ion, bromine ion or iodine ion. The equivalent circular diameter of the grains ranges from 0.04 to 2 microns.

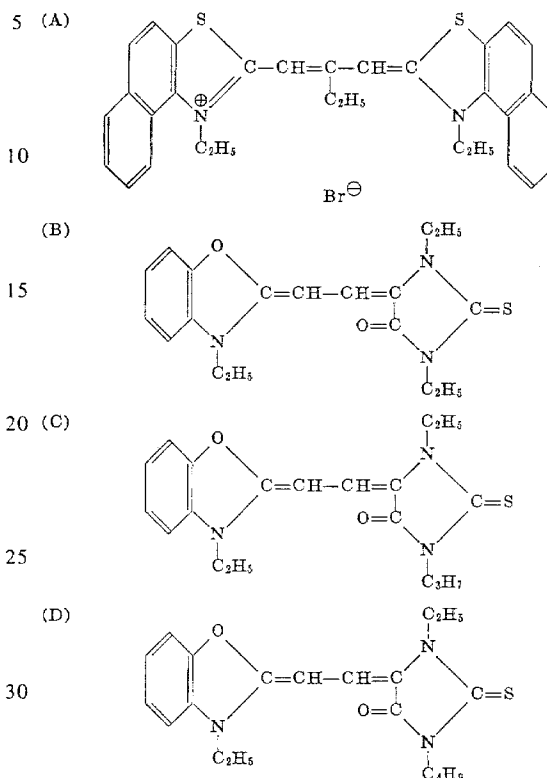
The degree of the effect of the invention greatly depends upon the properties of the silver halide emulsion, and a silver chlorobromide emulsion or a silver chlorobromiodide emulsion containing at least 30 mol percent of chlorine ion is especially useful. In addition, for the objects of the invention, preferably a silver halide photographic emulsion containing grains whose grain diameter distribution mode is less than 0.8μ is especially useful. Furthermore, silver halide grains in which at least 80 percent by weight have a crystal habit with a (1,0,0) face are preferable. The emulsions to be used in the invention are preferably chemically sensitized using reduction sensitization (U.S. Pat. Nos. 2,518,698, 2,419,974, 2,983,610, etc.), sulfur sensitization (U.S. Pat. Nos. 1,574,944, 2,278,947, 2,440,206, 2,410,689, 3,189,458, 3,415,649, etc.) or gold sensitization (U.S. Pat. Nos. 2,540,085, 2,597,856, 2,597,915, 2,399,083, etc.). It is especially preferable to employ the group IIb metal salts (e.g., a cadmium salt (e.g., nitrate, chloride), a mercury salt, (e.g., chloride, etc.), the group VIII metal salts (e.g., a rhodium salt, an iridium salt, a nickel salt, etc. refer, for example, to U.S. Ser. No. 219,047/72) or the group IVb metal salts (e.g., a lead salt (e.g., nitrate, chloride), etc.). The group IIb metal salts (e.g., cadmium chloride, zinc chloride, etc.) may be used as well.

Typical and specific examples of dyes which can be used in the invention will be illustrated hereinafter. This, however, is not intended to limit the invention in any way.





The chemical structural formulae of the comparative dyes used in the experiments conducted to explain the objects of the invention are given below.



35 Examples including comparative experiments of the present invention will be illustrated hereinafter.

EXAMPLE 1

A silver chlorobromide emulsion was prepared in the conventional manner. The chlorine ion content of the grains was 83 mol percent, and the mode of grain diameter distribution was 0.6 μ . Most of the grains had the (1,0,0) face. The silver content of the resulting emulsion was 1.3 mol/kg. 500 grams of the emulsions were weighed out in each pot and heated to 40°C to melt the emulsions. To the emulsions were further added 20 cc of a 1 M CdCl₂ solution. While stirring, each dye given in Table I was added to the emulsion as a methanol solution. After leaving for 15 minutes while stirring at 40°C, 10 cc of a 1 percent aqueous solution of sodium dodecylbenzenesulfonate and 10 cc of a 2 percent aqueous solution of 2,4-dichloro-6-hydroxy-S-triazine were added thereto. Each of the resulting emulsions was then applied to a cellulose acetate film in a dry thickness of about 4 μ to obtain samples. Each of the resulting samples was slit into a strip and wedgewise exposed to light from tungsten light source of 2854°K through a Wratten N058B green filter, a Wratten N025A red filter or a SC-42 yellow filter (made by the Fuji Photo Film Co., Ltd.), then developed for 20 minutes in a developer prepared by diluting the developer having the following composition with water in 1:1 by volume ratio.

Composition of the Developer

65	Water (about 50°C)	500 cc
	Metol	3 g
	Anhydrous Sodium Sulfite	45 g
	Hydroquinone	12 g
	Sodium Carbonate Hydrate	80 g
	Potassium Bromide	2 g
	Water to make	1000 cc

Thereafter, the strips were fixed in the conventional manner, and washed with water. After drying, the photographic density was measured using a densitometer made by the Fuji Photo Film Co., Ltd. to determine relatively the red filter sensitivity (Sr), the green filter sensitivity (Sg) and the yellow filter sensitivity (Sy) at the optical density of [fog + 0.5]. The results obtained are given in Table 1.

On the other hand, the spectrogram of each sample was determined using a spectrograph containing a reflection-type diffraction grating. The results obtained are shown by the curves 1 to 11 in FIGS. 1 to 6.

In order to demonstrate the effective influence of the combined use of the merocyanine dyes and the carbocyanine dyes of the invention on the gamma in the red sensitive wavelength region, the following sensitometry was conducted.

Wedgewise exposure was conducted using a monochromatic light source corresponding nearly to the sensitization maximum in the red sensitive wavelength region, and the same development, fixation and measurement of density as described above were effected to obtain H and D curves. The slope of the straight line portion thereof was determined, which was regarded as the

Table 1

No.	Merocyanine Dye Used	Carbocyanine Dye Used	Photographic Characteristics				Spectro- gram
			Sr	Sg	Sy	Fog	
1	(IC)	—	cc (mol con- centration)	cc (mol con- centration)			
			80	—	80	83	0.26
			(2×10 ⁻³)				
	—	(IIA)	120	—	100	100	0.27
			160	—	117	117	0.33
				20	*	40	0.22
	(IC)	(IIA)	(5×10 ⁻⁴)	40	112	45	0.22
				80	107	42	0.25
				40	145	80	0.19
	—	(IIA)	40	40	145	100	126
				40	135	100	132
2	(B)	—	80	—	*	40	44
			(2×10 ⁻³)				
			120	—	*	40	44
	—	(A)	160	—	*	35	31
				20	*	45	0.35
			(5×10 ⁻⁴)	40	107	60	0.25
	(B)	(A)	80	—	118	*	60
			40	—	141	*	66
			do.	—	85	40	56
	—	(A)	120	—	42	40	50
				do.	31	32	40
				do.	71	40	61
3	(B)	(IIA)	40	—	60	43	57
			80	—			
			120	—	35	37	44
	(IC)	(A)	40	—	117	63	100
			80	—	107	85	105
			120	—	83	104	120
	—	(IIC)	40	—	25	*	16
			(1×10 ⁻³)				
			80	—	32	*	20
	(IC)	(IIC)	40	—	72	94	110
			120	—	100	100	132
				do.			
4	(B)	(IIC)	40	—	40	42	60
			80	—			
			120	—	25	39	50
	(IC)	(IIC)	40	—			
			80	—			
			120	—			
	—	(IIC)	40	—			
			80	—			
			120	—			
	(IC)	(IIC)	40	—			
			80	—			
			120	—			

* Too small to measure accurately.

gamma value. The results obtained are shown in Table 2.

It is believed that the excellent advantages of the invention as enumerated below can be fully understood

Table 2

No.	Merocyanine Dye Used	Carbocyanine Dye Used	Wavelength of Exposure	gamma
	cc (mol con- centration)	cc (mol con- centration)	nm	
7	—	(IIA)	20 (5×10^{-4})	680 2.14
			40	do. 3.22
			80	do. 3.13
	(IC)			
	40 (2×10^{-3})	(IIA)	40	do. 3.64
	80		do.	do. 4.01
	120		do.	do. 4.30
8	(B)			
	40 (2×10^{-3})	(IIA)	40	680 2.88
	80		do.	do. 2.80
	120		do.	do. 2.08
9	—	(A)	20 (5×10^{-4})	680 0.88
			40	do. 1.14
			80	do. 2.72
	(IC)	(A)	40	do. 1.20
	80		do.	do. 1.38
	120		do.	do. 0.58
10	(B)	(A)	40	680 1.22
	80		do.	do. *
	120		do.	do. *
11	—	(IIC)	40	
			(1×10^{-3})	650 1.80
			80	do. 1.72
	(IC)	(IIC)	40	do. 3.08
	80		do.	do. 3.56

* ... Too small to measure accurately.

Furthermore, the results given in Table 3 were obtained in the same manner as described above. It can be understood from the above results that, in the merocyanine dyes in accordance with the invention, the variation in sensitivity due to the change of the substituent at the nitrogen atom in the thiohydantoin nucleus is reduced by the introduction of the sulfo group-containing alkyl group into the oxazole nucleus.

Table 3

No.	Merocyanine Dye Used	Sy	Fog	Stain
	cc (mol con- centration)			
12	(IC)	120 (2×10^{-3})	100 0.27	Nothing
		160	117 0.33	do.
13	(IF)	120 (2×10^{-3})	110 0.27	Nothing
		160	120 0.30	do.
14	(IG)	120 (2×10^{-3})	90 0.29	Nothing
		160	85 0.32	do.
15	(B)	120 (2×10^{-3})	44 0.27	Nothing
		160	31 0.35	do.
16	(C)	120 (2×10^{-3})	100 0.30	Extremely great
		160	110 0.34	do.
17	(D)	120 (2×10^{-3})	22 0.30	do.
		160	10> 0.45	do.

from the above results. That is,

1. a silver halide photographic emulsion with excellent contrast can be obtained;
2. high panchromatic sensitivity, especially high red sensitivity can be obtained;
3. stains can be reduced;
4. the fogging level can be maintained at a low level by the combination of at least two dyes; and the like.

EXAMPLE 2

A silver chlorobromiodide was prepared in the conventional manner (the chlorine ion content: 30 mol percent, the iodine ion content; 2 mol percent). 500 grams of the emulsions were weighed out in each pot and heated to 40°C to melt the emulsions. While stirring, each dye shown in Table 4 was added to the emulsion as a methanol solution. After leaving for 10 minutes while stirring at 40°C, 10 cc of a 1 percent aqueous solution of sodium dodecylbenzenesulfate and 10 cc of a 2 percent aqueous solution of 2,4-dichloro-6-hydroxy-S-triazine were added thereto. Each of the resulting emulsions was then applied to a cellulose acetate film in a dry thickness of about 4 μ to obtain samples.

Sensitometry was conducted according to Example 1 to obtain the results given in Table 4.

Table 4

No.	Merocyanine Dye Used	Carbocyanine Dye Used	Photographic Characteristics		
			Sr	Sg	Fog
	cc. (mol con- centration)	cc. (mol con- centration)			
12	(IA)	—	*	100	0.28
	80 (2×10^{-3})		*	107	0.29
	120				

Table 4—Continued

No.	Merocyanine Dye Used	Carbocyanine Dye Used		Photographic Characteristics		
		cc. (mol concentration)	cc. (mol concentration)	Sr	Sg	Fog
13	—	(IIA)	40 (5×10^{-4})	100	*	0.20
	(IA)	80	(IIB)	160	*	0.22
	(IB)	80	(IIB)	170	112	0.23
	(2 $\times 10^{-3}$)	—	do.	*	100	0.27
	120	(IID)	40 (1×10^{-3})	*	117	0.29
	—	(IIB)	80 (1×10^{-3})	71	*	0.23
14	(IB)	80	(IID)	80	*	0.25
	(ID)	80	40	96	120	0.29
	(2 $\times 10^{-3}$)	—	—	*	76	0.25
	120	(IIE)	20 (1×10^{-3})	*	104	0.25
	—	(IIE)	40 (1×10^{-3})	56	50	0.17
	(ID)	80	40	117	98	0.22
15	(IF)	80	(IIE)	80	141	0.20
	(2 $\times 10^{-3}$)	120	(IIE)	120	152	0.19
	120	do.	40	117	152	0.22
16	(IE)	80	—	117	178	0.21
	(2 $\times 10^{-3}$)	120	—	*	126	0.26
	160	(IIF)	40 (1×10^{-3})	*	132	0.29
(IE)	80	(IIF)	40	*	142	0.35
	120	(IIF)	40	83	31	0.22
	120	(IIF)	do.	100	132	0.25
				122	152	0.35

* ... Too small to measure accurately.

EXAMPLE 3

Of the samples obtained in Example 1, the sample used in Experiment No. 1 and No. 5 were wedgewise exposed as described in Example 1 and developed for 2 minutes at 20°C using an infectious developer which can be used for lithographic materials. Thus, images with a high panchromatic sensitivity, less stains and sharp toe-gradation could be obtained (see, for example, the paper by J.A.C. Yule reported in Journal of Franklin Institute, vol. 239, pp.221-230 (1945).

Composition of the Developer

Water (about 30°C)	500 cc
Anhydrous Sodium Sulfite	30 g
Paraformaldehyde	7.5 g
Acid Sodium Sulfate	2.2 g
Boric Acid	7.5 g
Hydroquinone	22.5 g
Potassium Bromide	1.6 g
Water to make	1000 cc

The sensitizing dyes used in the invention can be used preferably in an amount of from 1×10^{-6} mol to 5×10^{-3} mol per mol of silver depending upon the properties of silver halide emulsion used. The molar ratio of the carbocyanine dyes to the merocyanine dyes used in the invention is preferably from 1/10 to 1 to 5 to 1. The sensitizing dyes can be added as solution of a water-miscible organic solvent (e.g., methanol, ethanol, pyridine, acetone, cellosolve, etc.) or as an aqueous solution. In addition, conventional procedures employed by those skilled in the art can be applied.

The sensitizing dyes used in the invention can be used together with other sensitizing dyes such as the simple merocyanine dyes and dimethine merocyanine dyes included in the description of U.S. Ser. No. 236175 (1972), the monomethine cyanine dyes included in the description of U.S. Ser. No. 219047 (1972), trimethine cyanine dyes and pentamethine cyanine dyes, as long

as special anti-optical sensitization is not produced.

The complete emulsions prepared by the invention are applied to an appropriate support such as films, e.g., cellulose acetate films, cellulose acetate butyrate films, polyester films and other plastic films, papers such as baryta paper, polyolefin-coated papers, paper substitutes; glass plates; plastic plates, and the like.

The photographic effect of the photographic materials produced using the photographic emulsion of the invention is the same whether processed by continuous processing using an autodeveloping machine or using manual development processing as conventionally conducted.

The silver halide photographic light-sensitive materials obtained in the invention are especially useful for photographic arts materials, facsimile materials, micro-film materials, materials for COM system, a super-fine grain material for the production of IC or LSI or for holography, wherein especially a panchromatic sensitivity and a contrasty gradation are required.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

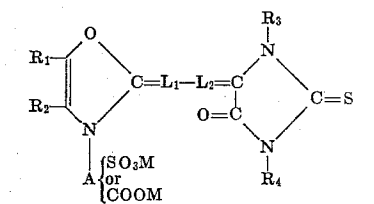
What is claimed is:

1. A silver halide photographic emulsion sensitized with the combination of (1) at least one dimethine merocyanine dye wherein the carbon atom at the 2-position of an oxazole nucleus bearing an alkyl group containing a sulfo or a carboxyl group on the nitrogen atom at the 3-position thereof and the carbon atom at the 5-position of a 2-thiohydantoin nucleus bearing a hydrogen atom or an alkyl group on the nitrogen atom at the 1- and 3-positions thereof are connected with each other through a dimethine chain, and (2) at least one of a J-band type carbocyanine dye comprising two cyanine nuclei joined by a trimethine chain selected

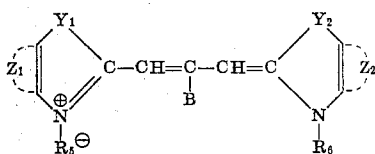
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from the group consisting of a naphthothiazole nucleus, a naphthoselenazole nucleus, a benzothiazole nucleus or a benzoselenazole nucleus and the carbon atom at the 2-position of two of said cyanine nuclei is attached to a mesoalkyl-substituted trimethine chain at opposite ends of said chain, at least one of said cyanine nuclei having a sulfo group-containing alkyl group attached to the nitrogen atom at the 3-position thereof.

2. The silver halide photographic emulsion as claimed in claim 1, wherein said dimethine merocyanine dye is represented by the following general formula;



wherein R_1 and R_2 each represents a hydrogen atom, a lower alkyl group or an aryl group, or, when taken together, R_1 and R_2 represent the atoms capable of forming an aromatic ring of the benzene series or the naphthalene series, R_3 and R_4 each represents a hydrogen atom or an alkyl group, L_1 and L_2 each represents a methine group, A represents a divalent aliphatic group and M represents a cation group, and said carbocyanine dye is represented by the following general formula;



wherein Y_1 and Y_2 each represents a sulfur atom or a selenium atom, B represents a lower alkyl group having 3 or less carbon atoms, Z_1 and Z_2 each represent the atoms necessary to complete an aromatic ring of the benzene series or the naphthalene series, R_5 and R_6 each represents a lower alkyl or sulfo-containing alkyl group, at least one of R_5 and R_6 being a sulfo-containing alkyl group.

3. The silver halide photographic emulsion as claimed in claim 1, wherein said emulsion contains silver chlorobromide or silver chlorobromiodide grains whose chlorine ion content is at least 30 mol percent, the mode of the grain diameter distribution is 0.8μ or less than 0.8μ , and at least 80 percent by weight of the grains have the crystal habit with a (1,0,0) face.

4. The silver halide photographic emulsion as claimed in claim 1, wherein the emulsion additionally contains a group IIb metal salt, a group VIII metal salt or a group IVb metal salt.

5. The silver halide photographic emulsion as claimed in claim 2, wherein said lower alkyl group for R_1 and R_2 is a methyl group or an ethyl group, wherein said aryl group for R_1 and R_2 is a phenyl group, a tolyl group, or a sulfophenyl group, wherein said aromatic ring of the benzene series formed by R_1 and R_2 forms a benzoxazole nucleus, or a substituted benzoxazole

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nucleus wherein the substituent is an alkyl group, a halogen atom, a hydroxyl group, an alkoxy group, an aryl group and an acetoxy group, and wherein said aromatic ring of the naphthalene series formed by R_1 and R_2 forms an α -naphthoxazole nucleus, a β , β -naphthoxazole nucleus, or a β -naphthoxazole nucleus, wherein said alkyl group for R_3 and R_4 is a methyl group, an ethyl group, a 2-propenyl group, a hydroxyalkyl group, an acetoxyalkyl group, an aminoalkyl group, a carboxyalkyl group, a sulfoalkyl group, or an aralkyl group, wherein said methine groups for L_1 and L_2 represent $=CH-$ or



in which W is an alkyl group, a hydroxyalkyl group, a carboxyalkyl group, an aryl group or an alkoxy group, wherein A is an ethylene group, a propylene group, a butylene group, an isopropylene group, or a propenylene group, wherein M is a sodium ion, an ammonium ion, a hydrogen ion, or a thiuronium ion, wherein the ring of the benzene series formed by Z_1 and Z_2 is a benzothiazole nucleus, a substituted benzothiazole nucleus wherein the substituent is a halogen atom, an alkoxy group, or an alkyl group, a benzoselenazole nucleus, or a substituted benzoselenazole nucleus wherein the substituent is an alkyl group, an alkoxy group, a hydroxy group, or an aryl group and wherein the aromatic ring of the naphthalene series formed by Z_1 and Z_2 is a naphthothiazole nucleus or a naphthoselenazole nucleus, wherein the alkyl group for R_5 and R_6 is a methyl group, an ethyl group, a propyl group, a propenyl group, a hydroxyalkyl group, an amidoalkyl group, an acetoxyalkyl group, or a carboxyalkyl group, and wherein said sulfo group-containing alkyl group for R_5 and R_6 is a sulfoethyl group, a sulfopropyl group, a 3-sulfobutyl group, a 4-sulfobutyl group, a 2-(3-sulfopropoxy)ethyl group, a 2-[2-(3-sulfopropoxy)ethoxy]ethyl group, or a sulfato propyl group.

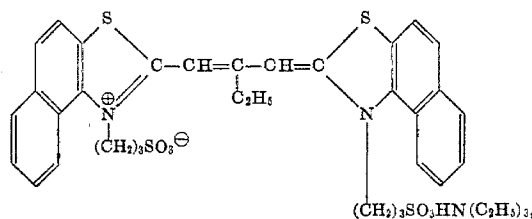
6. The silver halide photographic emulsion as claimed in claim 1 wherein said sensitizing dyes are each present in said emulsion in an amount ranging from 1×10^{-6} mol to 5×10^{-3} mol per mol of silver and wherein the molar ratio of said carbocyanine dye to said merocyanine dye ranges from 1/10:1 to 5:1.

7. A light sensitive photographic element comprising a support having at least one layer coated thereon of the silver halide photographic emulsion of claim 1.

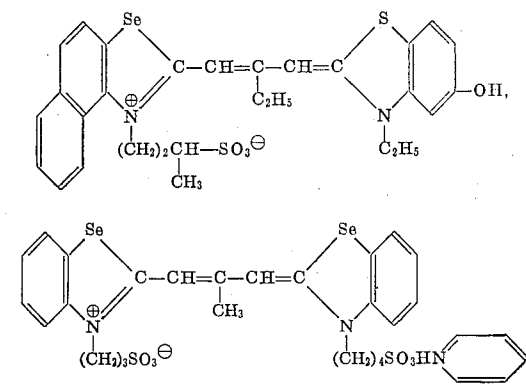
8. A light sensitive photographic element comprising a support having at least one layer coated thereon of the silver halide photographic emulsion of claim 2.

9. The light sensitive photographic element as claimed in claim 7 wherein said support is a synthetic resin film, a paper, a polyolefin coated paper, a paper substitute, a glass plate, or a plastic plate.

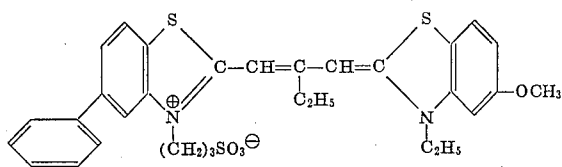
10. The silver halide photographic emulsion as claimed in claim 2 wherein said dye of the general formula II is selected from the group consisting of



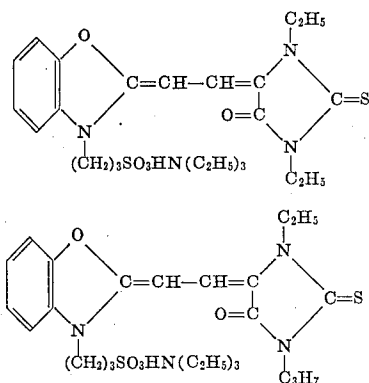
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and



and wherein said dye of the general formula I is selected from the group consisting of

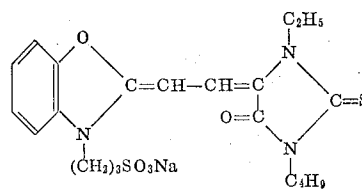


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and

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11. The silver halide photographic emulsion as claimed in claim 2, wherein Y_1 and Y_2 each represents a sulfur atom.

12. The silver halide photographic emulsion as claimed in claim 2, wherein Y_1 and Y_2 each represents a selenium atom.

13. The silver halide photographic emulsion as claimed in claim 2, wherein Z_1 and Z_2 each represents the atoms necessary to complete an aromatic ring of the benzene series.

14. The silver halide photographic emulsion as claimed in claim 2, wherein Z_1 and Z_2 each represents the atoms necessary to complete an aromatic ring of the naphthalene series.

15. The silver halide photographic emulsion as claimed in claim 2, wherein the substituent on A is SO_3M .

16. The silver halide photographic emulsion as claimed in claim 2, wherein the substituent on A is COOM.

17. The silver halide photographic emulsion as claimed in claim 1, wherein the sensitizing dye combination consists essentially of at least one of said dimethine merocyanine dyes and at least one of said J-band type carbocyanine dyes.

* * * * *