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PHOTOGRAPHIC EMULSION CONTAINING OPTICALLY DYE-SENSITIZED SILVER HALIDE GRAINS OF LESS THAN 0.2 MICRON

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U.S. Cl. 96—120 **12 Claims**

ABSTRACT OF THE DISCLOSURE

A photographic silver halide emulsion in which at least 95% of the silver halide grains are less than 0.2 micron or in which the mean grain size of the silver halide grains is less than 0.18 and which contains a sensitizing dye having an oxidation potential of less than 0.90 volt is disclosed.

BACKGROUND OF THE INVENTION

(1) Field of the invention

The present invention relates to a photographic silver halide emulsion and more particularly to a fine grain silver halide photographic emulsion which has been sensitized over the region from the specific absorption wave length region of the silver halide in the silver halide emulsion to a spectrally sensitized wave length region.

(2) Prior art

In the production of photographic light-sensitive elements, the technique for improving the light sensitivity of photographic emulsions is one of the most important techniques and various techniques have already been provided. These known techniques for improving light sensitivity generally can be divided into those in which the light sensitivity is improved during the preparation of the light-sensitive materials and those in which the light sensitivity is improved during the developing process. The latter technique is, however, accompanied with a tendency toward degradation of the granularity of silver images of the light-sensitive elements.

The first technique for light-sensitization is further divided generally into either chemical sensitization or spectral sensitiztaion (cf., E. K. Mees and T. H. James, The Theory of the Photographic Process, 3rd ed., par. 12, MacMillan Co. (1966).

Chemical sensitization includes such sensitizing methods as reduction sensitization, sulfur sensitization, noble metal sensitization (for example, salts of gold, platinum, palladium, iridinum or rhodium with thiocyanates), and combinations thereof. But, the application of any of these chemical sensitizations increases only the sensitivity of a specific absorption wave length region of the silver halide. On the other hand, spectral sensitization extends the photosensitive wave length region from the specific wave length region of absorption of silver halide toward the absorption of longer wave lengths.

When a photographic silver halide emulsion containing a sensitizing dye is subjected to spectral sensitization, the sensitivity of the silver halide emulsion in the specific absorption wave length region of silver halide is generally reduced. This phenomenon is called "desensitization" by a sensitizing dye. The extent of the desensitization is influenced largely by the composition of the silver halide emulsion used and the chemical structure of the sensitizing dye.

In cases in which the photographic silver halide emulsion used is not chemically ripened or is a silver iodobromide emulsion having internal sensitivity, the silver halide emulsion is, on the contrary, sensitized by a so-called desensitizing dye. This phenomenon is well known as the Capri-blue effect [see, for example, Tamura & Hada, "On the Desensitization of Silver Halide Emulsion by Dyes," Journal of Photographic Science, II (2), 87 (1967)].

However, the sensitivity of a silver halide emulsion obtained using the Capri-blue effect is considerably lower than that obtained by chemically sensitizing the silver halide emulsion. Thus, in practice this is not a valuable sensitizing method.

In the production of photographic light-sensitive elements, in order to improve the granularity of silver images, a fine grain silver halide emulsion is required. However, generally, if the grain size of silver halide is reduced, the light-sensitivity thereof is lowered.

Therefore, it is an important consideration in the production of photographic light-sensitive elements to prepare a silver halide emulsion having a silver halide of fine grain size and at the same time having a high sensitivity.

It has been found that when a dye having a specific nature is applied to a photographic silver halide emulsion containing silver halide crystals having the grain size less than a definite value, the light-sensitivity of the silver halide emulsion in the specific absorption wave length region of silver halide can be increased markedly in spite of that the silver halide emulsion had been subjected sufficiently to a chemical ripening procedure.

When a dye has an absorption in the wave length region from the blue region to the red region and the function of spectral sensitization, the sensitivity of a photographic silver halide emulsion can be markedly increased over the whole visible wave length regions by the addition of the dye to the silver halide emulsion.

Thus, an object of the present invention is to provide a photographic silver halide emulsion having fine silver halide grains and at the same time having a high sensitivity over a region from the specific absorption region of silver halide emulsion in which at least 95% of silver

SUMMARY OF THE INVENTION

The above-mentioned object of the present invention can be achieved by incorporating a dye having an oxidation potential value of less than 0.9 volt in a photographic silver halide emulsion in which at least 95% of silver halide grains contained in the silver halide emulsion have grain sizes less than 0.20 micron or in which the mean grain size of silver halide grains is less than 0.18 micron. By the aforesaid procedure, the sensitivity of the photographic silver halide emulsion can be uniformly increased over the region from the specific absorption wave length region of silver halide to the spectrally sensitized wave length region thereof.

Furthermore, it is particularly preferable in the present invention to incorporate the dye having the above-mentioned properties into a photographic silver halide emulsion which has been subjected to chemical ripening procedure.

The term oxidation potential used in the present specification, as measured by a voltammeter, means the potential at which the dye is oxidized by the anode (cf., P. Delahay, New Instrumental Methods in Electrochemistry, Interscience Publishers (1954), and L. Meites, Polarographic Techniques, 2nd ed., Interscience Publishers (1965).

The oxidation potential described in the present specification is the half-way potential of a voltage-current curve obtained by using a rotary platinum electrode and a saturated calomel electrode as the electrodes and also using sodium perchlorate as the supporting electrolyte. The dye is used as an acetonitrile solution having a concentration of from 1×10^{-4} mole to 1×10^{-6} mole [cf., A. Stanienda, Natur Wissenschaften, 47, 353 and 512 (1960)].

A series of observed oxidation potentials of dyes may have a deviation of about 100 millivolts by the influence of the contact potential difference between liquids, the temperature of measuring the electric resistance of the solution of dye, and the anions of the dyes. However, counter balancing the above-mentioned deviation by using an observed value of a dye as the standard (for example, dye I shown below), the reproducibility of the measurement of the oxidation potential can be secured.

As the photographic emulsions employed in the present invention, suitable emulsions are a silver iodobromide emulsion, a silver bromide emulsion, a silver chlorobromide emulsion, and a silver iodobromo-chloride emulsion. More particularly, a silver iodobromide emulsion and a silver bromide emulsion are preferred. The use of a silver chloride emulsion is, however, unprofitable in the present invention.

The particular sensitization effect of the present invention in the specific absorption wave length region of a silver halide emulsion depends on the grain size of silver halide particles in the emulsion, even when the halogen atom composition of the photographic emulsion is the same. Also, the sensitization of the photographic silver halide emulsion of the present invention can be applied to a sensitizing method such as a sulfur sensitization, a reduction sensitization and/or a noble metal sensitization. Also the sensitization in the present invention can be applied to a sensitizing method in a developing process. The particular sensitization effect of the present invention in the specific absorption region of silver halide is more marked as the size of the silver halide grains in the silver halide emulsion to which the dye is added is reduced below 0.20 micron. On the contrary, the larger the silver halide grains, the more the sensitization effect by the present invention is reduced. When the size of silver halide grains is 0.25 micron or larger, the sensitizing effect by the addition of the dye is lost or is converted into a desensitization function usually observed in the case of using a conventional sensitizing dye. For example, a silver iodobromide emulsion sufficiently subjected to chemical ripening was mixed with 1×10^{-3} mole/liter of a methanol solution of a thiacarbocyanine in an amount of 8 ml. per 100 g. of the silver halide emulsion and the resultant silver halide emulsion was applied to a support to provide a light-sensitive element, which was subjected to sensitometry using blue light. When the sensitivity obtained is compared with that of a sample prepared by using the same silver halide emulsion as above-mentioned and adding thiacarbocyanine to said silver halide emulsion, the following results are obtained according to the size of silver halide grains in the silver halide emulsion. The development in the experiments is conducted for 10 minutes at 20° C. as in Example 1 described hereinafter.

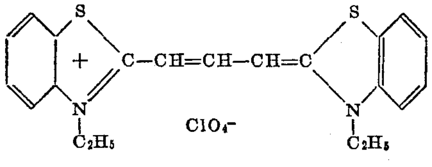
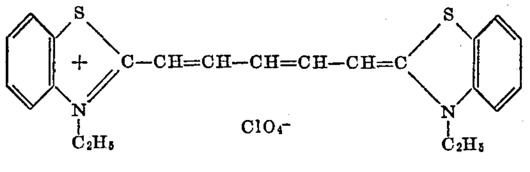
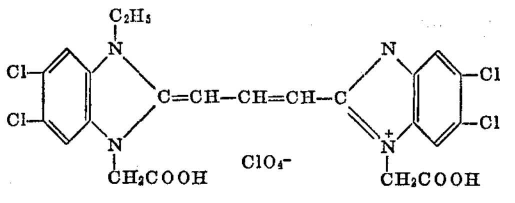
Mean grain size (in microns)	0.06	0.10	0.15	0.20	0.30
Sensitizing percent	330	200	145	100	85

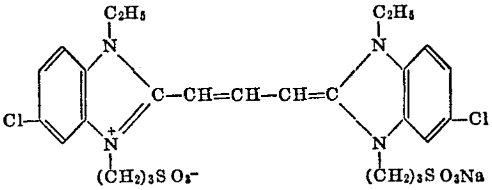
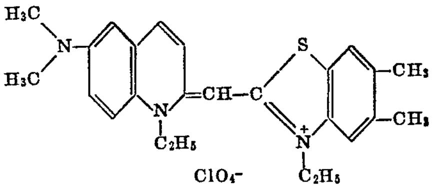
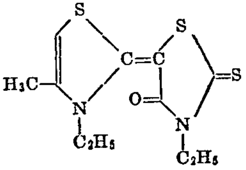
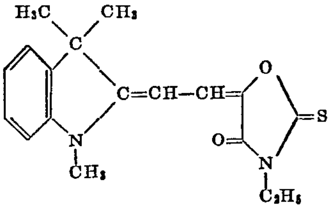
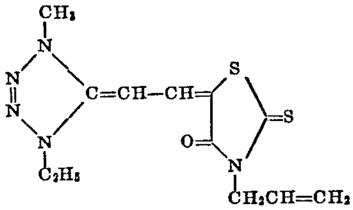
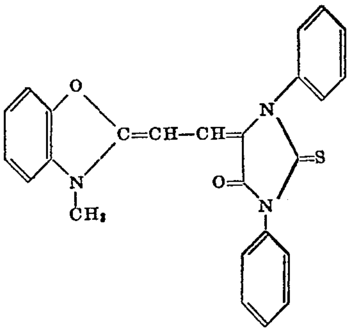
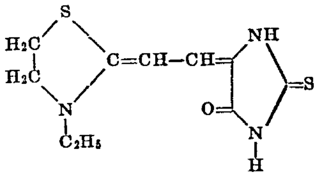
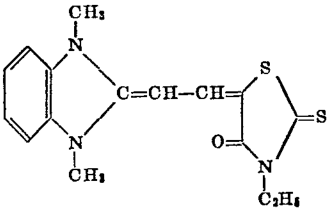
From the results it will be understood that the size of silver halide grains used in the emulsion is a very important factor for the specific effect of the present invention.

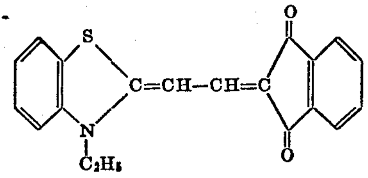
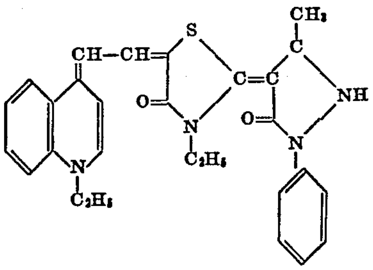
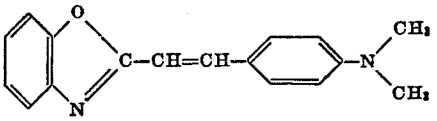
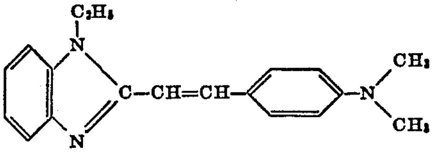
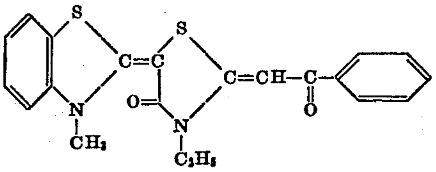
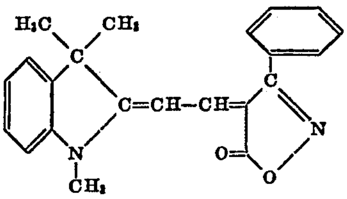
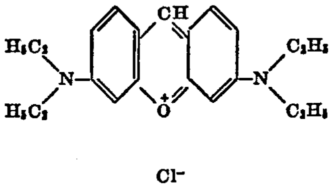
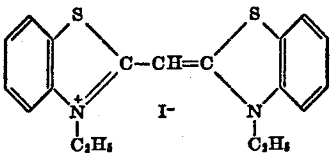
The sensitization effect of the present invention in the specific absorption wave length region is fundamentally different from the above-described Capri-blue effect. For example, when phenosafranine is incorporated in a silver iodobromide which was not subjected to a chemical ripening or which has a high internal sensitivity, the specific absorption wave length region of silver halide is sensitized, while the phenosafranine shows only a desensitization effect to the fine grain silver iodobromide emulsion employed in the present invention. Similarly, when 5,5',6,6'-tetrachlorobenzimidazolocarbocyanine is incorporated in a silver halide emulsion which shows a Capri-blue effect by the addition of phenosafranine, the silver halide emulsion shows no Capri-blue effect. On the other hand, when the aforesaid carbocyanine is incorporated in the fine grain silver iodobromide emulsion containing silver halide grains having the grain size as defined in the present invention, the additive causes a marked sensitization effect. This fact will be readily understood on considering that the oxidation potential of phenosafranine does not satisfy oxidation potential requirement for the present invention, whereas the oxidation potential of 5,5',6,6'-tetrachlorobenzimidazolocarbocyanine is 0.54 volt which is in the range suited for use in the present invention.

The dyes used in the present invention include merocyanine dyes, cyanine dyes, hemicyanine dyes, rhodacyanine dyes, trinuclear cyanine dyes, and styryl dyes. Suitable dyes for use have an oxidation potential lower than 0.90 volt.

The examples of the dyes used in the present invention are shown below together with the oxidation potentials although the dyes in the present invention shall not be limited to them only.

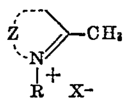
Dye		Oxidation potential (volt)
I		0.77
II		0.54
III		0.54

Dye		Oxidation potential (volt)
IV		0.48
V		0.61
VI		0.77
VII		0.72
VIII		0.52
IX		0.45
X		0.42
XI		0.33

Dye		Oxidation potential (volt)
XII		0.82
XIII		0.35
XIV		0.68
XV		0.61
XVI		0.67
	Comparative dye:	
A		1.01
B		1.18
C		1.25

The dyes used in the present invention can be prepared by known methods, that is, can be generally prepared as follows:

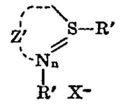
The trimethine dye, Dye I, can be prepared by condensing a quaternary ammonium salt represented by the general Formula I


(I)

and an ortho-formic acid ester in pyridine in the presence of a base such as triethylamine.

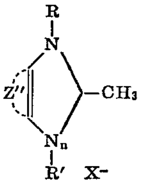
Also, the pentamethine dye, Dye II, can be prepared by using in the above described condensation reaction 1,3,3-triethoxypropene and the like instead of the ortho-formic acid ester.

Furthermore, the monomethine dye, Dye V, or Comparative Dye C can be prepared by condensing a quaternary ammonium salt intermediate product represented by the general Formula II shown below.


(II)

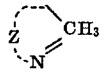
and the quaternary ammonium salt represented by the aforesaid general Formula I in a suitable solvent such as an alcohol (e.g., methanol or ethanol) or pyridine in the presence of a base such as triethylamine.

Also, the benzimidazolocarbocyanine dye, Dye II or IV, can be prepared by condensing a quaternary ammonium salt intermediate product represented by the following general Formula III


(III)

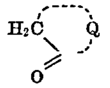
and an ortho-formic acid ester in nitrobenzene in the presence of a base such as triethylamine or condensing the said quaternary ammonium salt intermediate product and a chloral in an alcohol in the presence of an alcoholate.

The styryl base dye, Dye XIV or XV, can be prepared by condensing a compound represented by the following general Formula IV

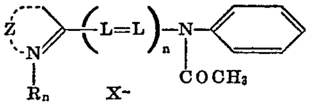

(IV)

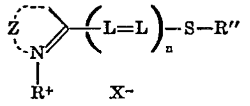
and a p-dialkylaminobenzaldehyde in the presence of zinc chloride.

Furthermore, merocyanine dyes, Dye VI, VII, VIII, IX, X, XI or XII, shown above, can be prepared by condensing a ketomethylene compound represented by the following general Formula V


(V)

and an intermediate product represented by the following general Formula VI or VII


(VI)


(VII)

in an alcohol (e.g. methanol or ethanol) or pyridine in the presence of a base such as triethylamine.

In the aforesaid general formulae, Z and Z′ each represents an atomic group necessary to complete a nitrogen-containing heterocyclic ring, such as a benzothiazole, a naphthothiazole, a benzoselenazole, a naphthoselenazole, a benzoxazole, a naphthoxazole, a quinoline, a benzimidazole, a thiazole, an oxazole, or a terazole ring; Z″ represents an atomic group necessary to complete a benzimidazole ring; R, R′, and R″ each represents an alkyl group such as a methyl group, an ethyl group, or a n-propyl group; a substituted alkyl group such as a β-hydroxyethyl group, a β-carboethoxyethyl group, a carboxymethyl group, a β-carboxyethyl group, a β-sulfoethyl group, a γ-sulfopropyl group, a δ-sulfobutyl group, a β-phenylethyl group, or an allyl group (or vinylmethyl group); or an aryl group; L represents a methine chain or a methine chain substituted by an alkyl group such as a methyl group, an ethyl group, and the like; X′ represents an anion; Q represents an atomic group necessary to complete a ketomethylene ring, such as a rhodanine nucleus, a hydantoin nucleus, a thiohydantoin nucleus, an oxazolidinone nucleus, or a pyrazolone nucleus; and *n* is 0, 1 or 2.

The above-mentioned dyes in the present invention can be used together with other additives such as stabilizers, antifoggants, sensitizing dyes, hardening agents, wetting agents, water-soluble high molecular weight compounds, e.g., gelatin or gelatin derivatives, film-denaturing agents, and couplers if desired. Also, it is especially suitable that the dye in the present invention be used as a dye having the above-mentioned specific sensitizing effect and a spectral sensitization function.

The photographic silver halide emulsion of the present invention can be applied to any suitable support such as a glass plate, a triacetyl cellulose film, a polyethylene terephthalate film, other plastic films, a plastic sheet, a baryta-coated paper, a resin-laminated paper, and the like.

The invention will be more practically described by referring to the following examples.

EXAMPLE 1

A silver iodobromide emulsion was prepared in a conventional manner and was subjected to physical ripening or chemical ripening in the conventional manner. The silver halide emulsion contained 1 mole percent of iodide ion and the mean size of the silver halide grains in the emulsion was 0.06 micron. Fifty grams (50 g.) of the silver halide emulsion was placed in a beaker and melted by heating the beaker in a bath at 40° C. A specific amount of a solution of the dye of the present invention having a concentration of 1×10^{-3} mole/liter was added to the molten emulsion with stirring and 7 ml. of the resultant emulsion was applied to a glass plate of cabinet size and dried.

The light-sensitive plate was exposed by optical wedge to a tungsten light of a color temperature of 2854° K. by means of a S-type sensitometer made by Fuji Photo Film Co., through a blue filter No. K–31 or a yellow filter No. K–12. Subsequently, the photographic plate was developed for 10 minutes at 20° C. in a developer having the following composition, and then fixed.

Developer composition:

Water	ml	500
Metol	g	0.3
Potassium pyrosulfite	g	1.4
Anhydrous sodium sulfite	g	38
Hydroquinone	g	6
Sodium carbonate monohydrate	g	22.5
Citric acid	g	0.7
Potassium bromide	g	0.9
Water to make 1000 ml.		

The optical density of the photographic plate thus treated was measured by using a S-type sensitometer made by Fuji Photo Film Co. and the results of the relative blue filter sensitivity, S*b*, and the relative yellow filter sensitivity, S*y*, at the point where the optical density was fog+0.2 are shown in the following table.

No.	Dye	Oxidation potential (volt)	Addition amount (ml.)	S*y*	S*y*
1	None			100	
	I	0.77	2	252	1,660
	I	0.77	4	380	2,890
2	II	0.54	0.2	490	660
	II	0.54	0.4	2,400	10,500
3	III	0.54	2	800	10,000
	III	0.54	4	630	10,000
4	IV	0.48	2	316	3,630
	IV	0.48	4	562	5,000
5	V	0.61	2	200	2,000
	V	0.61	4	200	2,340
6	VI	0.77	2	136	34
	VI	0.77	4	141	50
7	VII	0.72	2	250	660
	VII	0.72	4	250	1,150
8	VIII	0.52	2	240	635
	VIII	0.52	4	330	1,000
9	IX	0.45	2	240	790
	IX	0.45	4	400	1,590
10	X	0.42	2	1,180	2,340
	X	0.42	4	1,180	3,160
11	XI	0.33	2	562	2,520
	XI	0.33	4	562	2,350
12	XII	0.82	2	136	100
	XII	0.82	4	115	141
13	XIII	0.35	2	330	12,600
	XIII	0.35	4	330	14,100
14	XIV	0.68	2	895	562
	XIV	0.68	4	1,180	800
15	XV	0.61	2	167	50
	XV	0.61	4	200	100
16	XVI	0.67	2	142	50
	XVI	0.67	4	142	70
Control	A	1.01	2	100	
	A	1.01	4	100	
Control	B	1.18	1	31	
	B	1.18	2	<10	
	C	1.28	2	100	
	C	1.28	4	105	

EXAMPLE 2

The same procedure as used in Example 1 was followed using a silver chlorobromide emulsion. The bromine content in the silver halide emulsion used was 40 mole percent and the mean size of the silver halide grains in the emulsion was about 0.1 micron. The results are as follows.

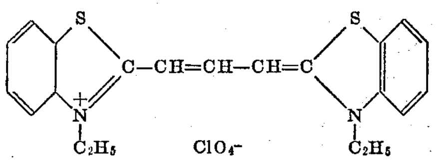
No.	Dye	Oxidation potential (volt)	Addition amount (ml.)	S*b*	S*y*
17	None			100	
	I	0.77	1	142	316
	I	0.77	2	160	316
18	X	0.42	1	560	830
	X	0.42	2	700	830

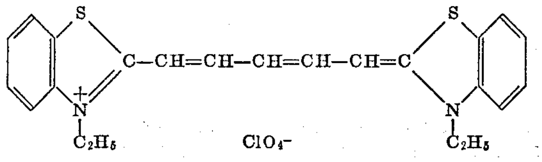
What is claimed is:

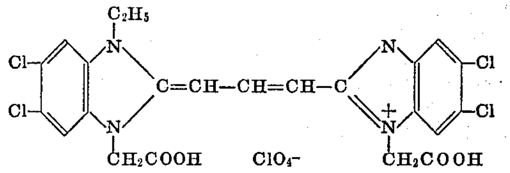
1. In a photographic negative silver halide emulsion containing a silver halide, excluding silver chloride, and a sensitizing dye, the improvement which comprises at least 95% of the silver halide having a grain size less than 0.2 micron, said dye having an oxidation potential of less than 0.90 volt and being a member selected from the group consisting of a merocyanine dye, a cyanine dye, a hemicyanine dye, a rhodacyanine dye, a trinuclear cyanine dye, and styryl dye.

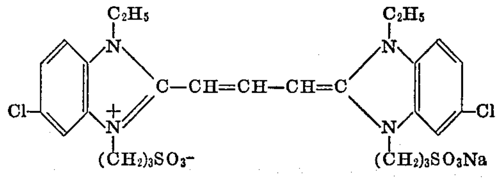
2. In a photographic negative silver halide emulsion containing a silver halide, excluding silver chloride, and a sensitizing dye, the improvement which comprises the silver halide having a mean grain size less than 0.18 micron, said dye having an oxidation potential of less than 0.90 volt, and being a member selected from the group consisting of a merocyanine dye, a cyanine dye, a hemicyanine dye, a rhodacyanine dye, a trinuclear cyanine dye and a styryl dye.

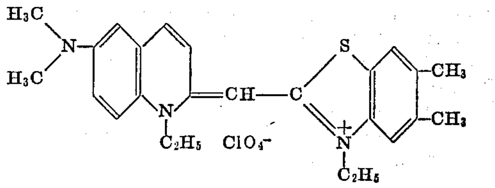
3. The photographic negative silver halide emulsion as claimed in claim **1**, wherein said dye is a member selected from the group consisting of:

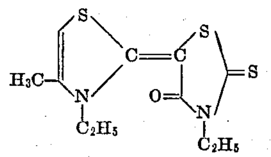


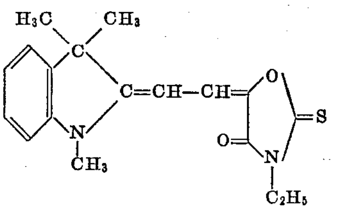


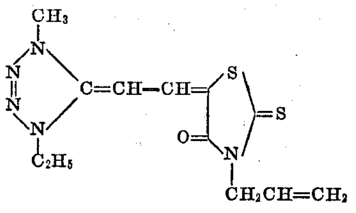


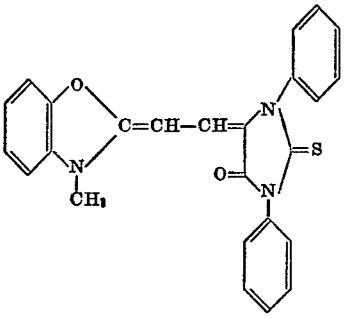


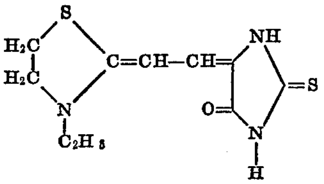


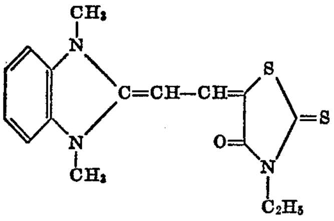


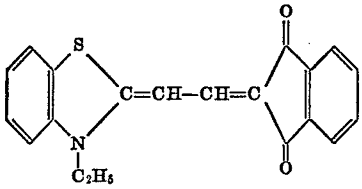


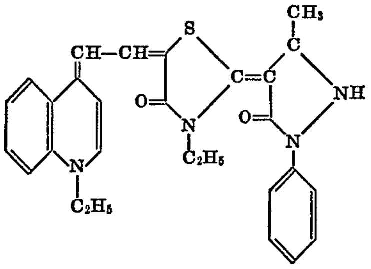


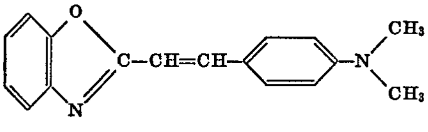


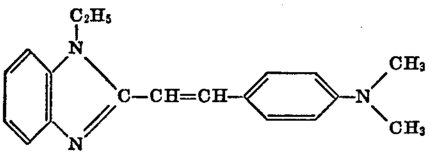












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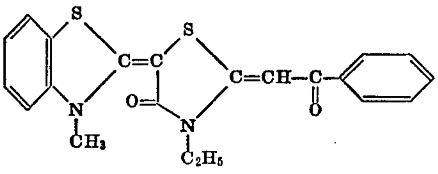
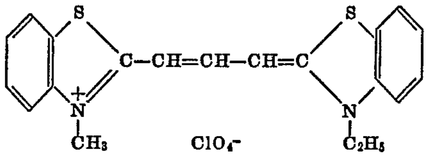
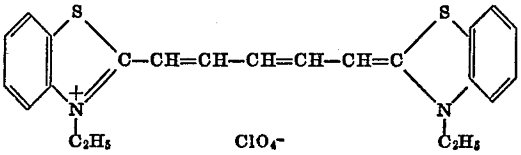
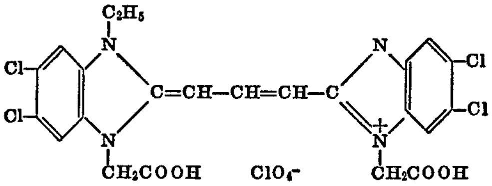
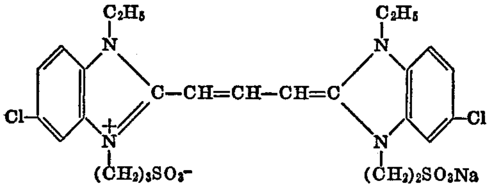


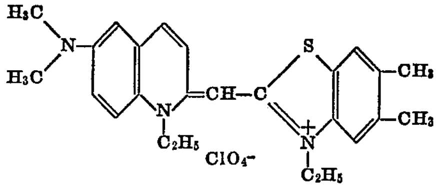
4. The photographic negative silver halide emulsion as claimed in claim **2**, wherein said dye is a member selected from the group consisting of:

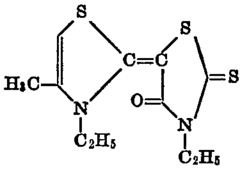


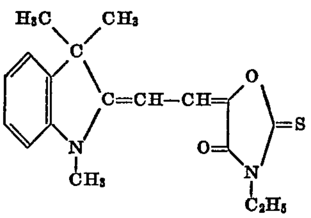


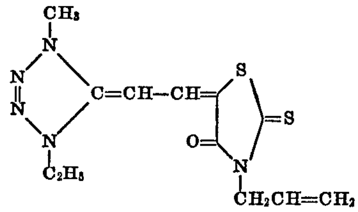


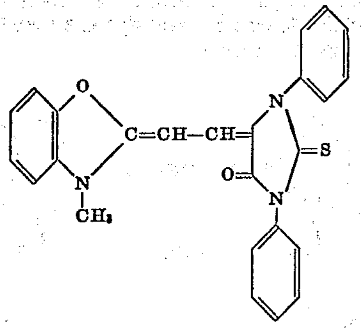


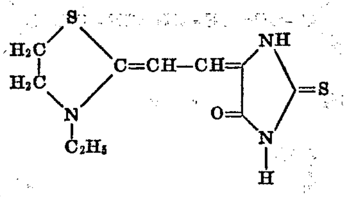


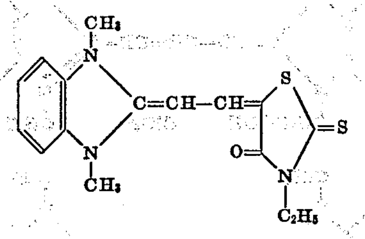


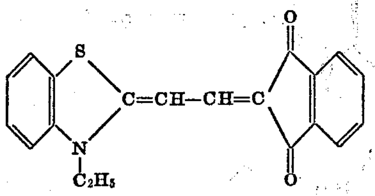


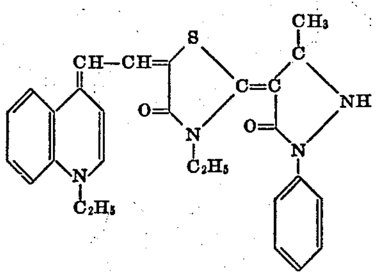


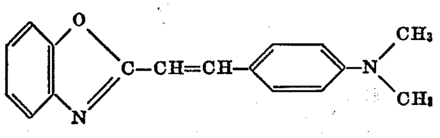


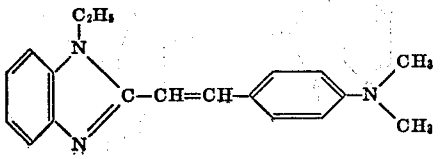












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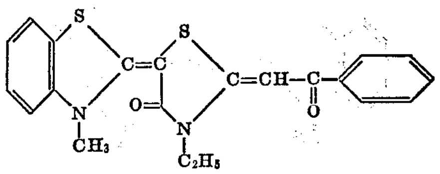

5. The photographic negative silver halide emulsion as claimed in claim **1**, wherein said emulsion has been subjected to chemical ripening.

6. The photographic negative silver halide emulsion as claimed in claim **1**, wherein said silver halide is silver iodobromide, silver bromide, silver chlorobromide or silver iodobromo-chloride.

7. In a photographic negative light-sensitive element comprising a support and one or more photographic silver halide emulsion layers coated thereon, the improvement which comprises at least one of the layers containing a photographic silver halide emulsion as claimed in claim **1**.

8. In a photographic light-sensitive element comprising a support and one or more photographic silver halide emulsion layers coated thereon, the improvement which comprises at least one of the layers containing a photographic silver halide emulsion as claimed in claim **5**.

9. The photographic negative silver halide emulsion as claimed in claim **2**, wherein said emulsion has been subjected to chemical ripening.

10. The photographic negative silver halide emulsion as claimed in claim **2**, wherein said silver halide is silver iodobromide, silver bromide, silver chloro-bromide or silver iodobromo-chloride.

11. In a photographic negative light-sensitive element comprising a support and one or more photographic silver halide emulsion layers coated thereon, the improvement which comprises at least one of the layers containing a photographic silver halide emulsion as claimed in claim **2**.

12. In a photographic light-sensitive element comprising a support and one or more photographic silver halide emulsion layers coated thereon, the improvement which comprises at least one of the layers containing a photographic silver halide emulsion as claimed in claim **9**.

References Cited

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J. TRAVIS BROWN, Primary Examiner

W. H. LOUIE, Jr., Assistant Examiner

U.S. Cl. X.R.

96—94, 127, 129, 137, 139, 140, 143

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,706,566 Dated December 19, 1972

Inventor(s) Keisuke Shiba et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In The Specification:

Column 2, line 14, delete "emulsion in which at least 95% of silver" and insert -- to the spectral sensitizing region.--

Signed and sealed this 24th day of December 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents