United States Patent Office 3,759,713 Patented Sept. 18, 1973

3,759,713

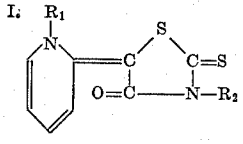
FOGGED, DIRECT-POSITIVE SILVER HALIDE EMULSION SUPERSENSITIZED WITH A MEROCYANINE DYE AND A CARBOCYANINE DYE

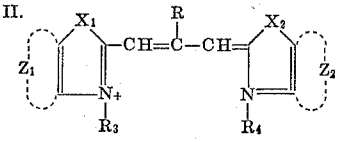
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No Drawing. Filed July 14, 1971, Ser. No. 162,612
Claims priority, application Great Britain, Aug. 14, 1970, 39,353/70
Int. Cl. G03c 1/08
U.S. Cl. 96—126 21 Claims

ABSTRACT OF THE DISCLOSURE

A photographic direct-positive silver halide emulsion is described wherein the silver halide grains have a central core of silver halide containing centers promoting the deposition of photolytic silver and over said core an outer shell of fogged silver halide and wherein said outer shell comprises absorbed thereto a 2-pyridine-rhodanine merocyanine dye of Formula I and a carbocyanine dye of Formula II

I. 

II. 

wherein:

R_1, R_2, R_3 and R_4 represent a saturated or unsaturated aliphatic group, a cycloaliphatic group or an aryl group,
X_1 and X_2 represent oxygen, sulphur, selenium or $N(R_5)$ wherein R_5 has the significance given for R_1–R_4,
Z_1 and Z_2 represent the atoms necessary to close a fused-on aromatic nucleus of the benzene series,
R is hydrogen, alkyl, aralkyl, or aryl, and
X is an anion but does not exist when one of R_3, R_4, and R_5 contains an anionic group.

The combination of dyes used has a supersensitizing effect on the emulsion. The total speed is markedly increased as compared with the use of either dye alone and less stain is produced.

The present invention relates to the spectral sensitization of direct-positive silver halide emulsions.

It is known that positive photographic images can be obtained without previously forming a negative silver image by the use of silver halide emulsions that have been pre-fogged by overall exposure to actinic radiation or by overall chemical fogging. Upon image-wise exposure of the prefogged emulsions the development centres formed by said fogging are destroyed at the exposed areas, but remain at the unexposed areas. By subsquent development by means of silver halide developers a direct-positive image is obtained.

Special types of direct-positive silver halide emulsions are known, in which the silver halide grains comprise a central core of silver halide having centres promoting the deposition of photolytic silver and an outer shell of silver halide, which has been fogged overall.

Photographic emulsions comprising in the interior of the silver halide grains, centres promoting the deposition of photolytic silver are known, e.g. from U.K. patent specifications 1,011,062 filed May 15, 1962, 1,151,781 filed Apr. 15, 1966 both by Eastman Kodak Co., and 1,027,146 filed Aug. 30, 1963 by Agfa AG.

According to U.K. patent specification 1,011,062 emulsions having ripening nuclei in the interior of the grains are prepared by admixture of a coarse-grained silver halide emulsion, which has been ripened chemically and comprises ripening nuclei at the surface of the grains, with a fine-grain silver halide emulsion followed by physical ripening of the mixture, whereby the large grains grow at the cost of the small grains so that the unripened fine-grain emulsion deposits around the ripened coarse-grain emulsion.

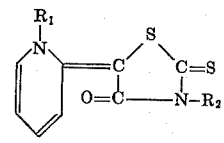
In United Kingdom patent specification 1,027,146 a process has been described and claimed, according to which silver halide emulsions are prepared having a narrow grain-size distribution and containing composite silver halide granules, whose internal structure is different from the surface structure. According to one embodiment of this process a fine-grained silver halide emulsion with narrow grain-size distribution is prepared first, whereupon the precipitation of the silver halide is interrupted and the surface of the silver halide nuclei is modified chemically or physically e.g. by treatment with reducing agents e.g. hydrazine and derivatives, ascorbic acid and formaldehyde, by treatment with noble metal salts e.g. gold salts or by exposure to actinic radiation, and finally precipitation of the same or another silver halide is continued.

By overall fogging the emulsions formed according to these U.K. patent specifications 1,011,062 and 1,027,146 before or after coating on a support, a photographic direct-positive silver halide emulsion can be obtained.

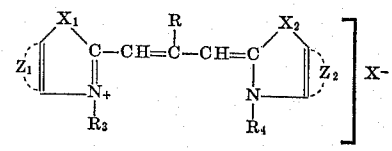
According to U.K. specification 1,151,781 there is provided a method of making a photographic direct-positive material, which comprises forming grains of a first light-sensitive silver salt, treating these grains so as to produce centres therein, which promote the deposition of photolytic silver, covering the treated grains with a layer of a second light-sensitive silver salt and fogging the resulting emulsion before or after coating on a support.

The speed of these types of direct-positive silver halide emulsions, which in the interior of the silver halide grains have centres promoting the deposition of photolytic silver, can be increased as is known e.g. from U.K. patent specification 1,186,718 filed Mar. 17, 1967 by Eastman Kodak Co. by means of Blue Speed Increasing (BSI) merocyanine dyes.

It has now been found that direct-positive emulsions that have a central silver halide core containing centres promoting the deposition of photolytic silver and over said core an overall fogged outer shell of silver halide, can be supersensitized by adsorption to said outer shell of a 2-pyridine-rhodanine merocyanine dye corresponding to the following General Formula I and carbocyanine dye corresponding to the following General Formula II

I. 

and

II. 

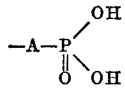
wherein:

R_1, R_2, R_3 and R_4 stand for a substituent of the type contained in cyanine dyes on the cyanine nitrogen atom such as an aliphatic group including a saturated aliphatic group, an unsaturated aliphatic group and a cycloaliphatic group e.g. alkyl, allyl, aralkyl, and cycloalkyl or an aryl group, which groups may carry sub-

stituents; more particularly an alkyl group such as methyl, ethyl, propyl, isopropyl, butyl, a substituted alkyl group such as β-hydroxyethyl, β-acetoxyethyl, carboxymethyl and carboxyethyl as described in the German patent specification 704,141 filed Mar. 8, 1938 by I. G. Farbenindustrie AG, sulphoalkyl as described in the United Kingdom patent specification 742,112 filed Oct. 23, 1952 by Agfa AG such as sulphoethyl, sulphopropyl, sulphobutyl, sulphatoalkyl as described in the French patent specification 1,149,769 filed May 14, 1956 by VEB Filmfabrik Agfa Wolfen such as sulphatopropyl and sulphatobutyl, the group

$$—A—CO—O—B—SO_2—OH$$

wherein A and B have the same significance as set forth in United Kingdom patent specification 886,271 filed Aug. 18, 1958 by Gevaert Photo-Producten N.V. such as a sulphocarbomethoxy-methyl group, a ω-sulphocarbopropoxymethyl group, a ω-sulphocarbobutoxy-methyl group, a p-(ω-sulphocarbobutoxy)-benzyl group, the group —A—W—NH—V—B wherein A, W, V and B have the same significance as set forth in United Kingdom patent specification 904,332 filed July 5, 1957 by Gevaert Photo-Producten N.V. such as a N-(methylsulphonyl)carbamylmethyl group, γ - (acetylsulphamyl)-propyl, a δ-(acetylsulphamyl)butyl group, the group



wherein A has the same significance as described in the United Kingdom patent specification 886,270 filed June 24, 1957 by Gevaert Photo-Producten N.V., cyclohexyl, allyl, benzyl including substituted benzyl such as carboxybenzyl and sulphobenzyl, and phenyl including substituted phenyl such as carboxyphenyl;

X_1 and X_2 stand for oxygen, sulphur, selendium or the group $N(R_5)$ wherein R_5 has the same significance as R_1–R_4,

Z_1 and Z_2 stand for the atoms necessary to complete a fused-on aromatic nucleus of the benzene series which may be substituted, e.g. by halogen, alkyl, substituted alkyl, alkoxy, alkylsulphonyl, sulphamoyl, etc.;

R stands for hydrogen, alkyl, aralkyl or aryl, and

X stands for an anion of the type contained in cyanine dye salts, such as chloride, bromide, iodide, perchlorate, benzene sulphonate, toluene sulphonate, methyl sulphate, ethyl sulphate, etc. or X does not exist when one of R_3, R_4, and R_5 itself contains an anionic group, in which case the dye is a betaine dye.

By the use of this combination of sensitizers the total speed of the direct-positive emulsion is markedly increased as compared with the use of either sensitizer alone and less stain is produced so that lower minimum densities i.e. brighter whites are obtained.

Direct-positive silver halide emulsions having a central core of silver halide containing centres promoting the deposition of photolytic silver and over said core an outer shell of silver halide that has been fogged, can be obtained by the following steps:

(1) the formtaion of silver halide grains by mixing in an aqueous gelatin solution a dissolved water-soluble silver salt and a dissolved water-soluble alkali metal halide salt,

(2) the interruption of the precipitation,

(3) treatment of the silver halide grains (cores) so as to produce centres which promote the deposition of photolytic silver,

(4) the further mixing of silver and halide salt solutions thus forming a shell of silver halide around the cores, and

(5) the fogging of the resulting silver halide emulsion at the surface of the silver halide grains to such an extent that after a sufficient image-wise exposure of the emulsion layer to radiation to which the grains are sensitive, a direct-positive silver image can be obtained by treatment of the exposed emulsion in a silver halide developer.

The precipitation of the silver halide is preferably carried out by simultaneous addition of the halide salt solution and the silver salt solution to the gelatin solution and keeping the pAg value as constant as possible during precipitation. Thus it is possible to form emulsions having an extremely narrow grain size distribution i.e. the silver halide grains have a substantially uniform diameter, preferably at least 95% by weight of said grains having a diameter that is within about 40% of the mean grain diameter.

In preparing direct-postiive silver halide emulsions having a central silver halide core containing centres promoting the deposition of photolytic silver and over said core a fogged outer shell of silver halide, the said silver halide cores may be treated physically or chemically according to any of the known procedures for producing the said centres promoting the deposition of photolytic silver. Such centres are produced preferaby by chemical sensitization and any of the usual methods may be used therefor. Thus the cores may be digested with naturally active gelatin or with a labile sulphur compound. The cores may be sensitized chemically with noble metal sensitizers, e.g. compounds of gold, platinum, palladium, and iridium such as gold(III)chloride, potassium chloroaurate, and ammonium chloropalladate or with reduction sensitizers such as tin(II)salts, thiourea dioxide, and polyamines or with both a reduction sensitizer and a noble metal sensitizer. Gold sensitization preferably occurs by means of a mixture of a water-soluble gold salt such as gold(III)chloride and a thiocyanate froming complexes with gold and having a solvent action on the silver halide grains e.g. alkali metal and ammonium thiocyanates. Reduction sensitization may also occur by digestion of the cores at low pAg values (J. Phot. Sci. 6, 33 (1958)). The centres promoting the deposition of photolytic silver may also be produced by subjecting the cores to fogging by exposure to radiation of either low or high intensity.

The outer shell of silver halide provided over the silver halide core of the silver halide grains is prepared by precipitating silver halide around the silver halide cores formed, which have been treated previously physically or chemically as described above so as to produce centres promoting the deposition of photolytic silver. The outer shell is then fogged uniformly at the surface to such an extent that it is developable by conventional surface image developing compostions. Fogging may occur by exposure, before or after coating of the emulsion, to actinic radiation but preferably fogging occurs by chemical means. Chemical fogging can be effected by chemically sensitzing to fog using one of the chemical sensitizing methods outlined above. Fogging can be effected successfully by means of reducing agents e.g. hydrazine, hydroxylamine, tin(II)salts such as tin(II)chloride, ascorbic acid, formaldehyde, thiourea dioxide, etc. Fogging of the silver halide shell may also be effected by high pH and/or low pAg silver halide precipitating conditions.

According to a special embodiment of the present invention the centres promoting the deposition of photolytic silver in the interior of the silver halide grains are produced by chemical sensitization with a gold compound together with a reduction sensitizer e.g. thiourea dioxide, also called formamidine sulphinic acid and derivatives thereof, whereas the external fogging of the composite silver halide granules occurs with the same reduction sensitizer. The use of thiourea dioxide or formamidine sulphinic acid and derivatives thereof is known from United Kingdom patent specification 789,823 filed Apr. 29,

1955 by Gevaert Photo-Producten N.V. and from United States patent specifications 2,983,609 and 2,983,610 of Charles F. H. Allen and Wesley G. Lowe and of Charles F. H. Allen, Wesley G. Lowe and John Sagal both issued May 9, 1961.

Further details as regards the preparation of these types of direct-positive emulsions can be found in the U.K. patent specifications referred to above.

The merocyanine and carbocyanine dyes used according to the present invention are added to the silver halide emulsion preferably after fogging of the outer silver halide shell. They can be used in widely varying concentrations but are employed generally at concentrations in the range of 50 mg. to 500 mg., preferably 100 mg. to 300 mg. per mole of silver halide.

The composite silver halide granules formed may contain silver chloride, silver bromide, or silver iodide or mixtures thereof. For example, a core of silver bromide can be coated with a shell of silver chloride or a mixture of silver bromide and silver iodide, or a core of silver chloride can have deposited thereon a shell of silver bromide. However, the composite silver halide granules preferably have an interior core of silver bromide, around which silver bromide has been deposited.

Gelatin is used preferably as vehicle for the composite silver halide granules but like in other silver halide emulsions the gelatin may be replaced wholly or partly by other hydrophilic colloids, e.g. colloidal albumin, zein, agar-agar, polyvinyl alcohols, polyvinyl acetals, hydrolyzed cellulose esters or ethers, etc.

In addition to the above sensitizing dyes, the direct-positve silver halide emulsions comprising in the interior of the silver halide grains centres promoting the deposition of photolytic silver may also comprise all kinds of known emulsion ingredients for direct-positive emulsions for example wetting agents, development accelerators, optical brightening agents, hardeners, stabilizers, etc They may comprise selenium compounds as described in copending application No. 15472/70 filed Apr. 1, 1970 by Gevaert-Agfa N.V. for increasing the reversal speed of the direct-positive silver halide elements.

The direct-positive emulsions sensitized spectrally in accordance with the present invention can be coated on any of the wide variety of supports. Typical supports include, e.g. cellulose nitrate film, cellulose acetate film, polyvinyl acetal film, polystyrene film, polyethylene terephthalate film and films of other polyesters as well as paper, paper coated with e.g. polyethylene or polypropylene, glass and metal.

Spectrally sensitized direct-positive silver halide emulsions according to the present invention can be employed for colour photography, e.g. emulsions containing colour-forming couplers or emulsions to be developed by solutions containing couplers. The emulsions may be used in silver halide diffusion transfer processes and in colour transfer processes. They can be processed in monobath processes or in stabilization type processes.

The spectrally sensitized emulsions according to the invention are also developable by so-called lith-developers, as described in French patent specification 2,042,173 filed Mar. 24, 1970 by Gevaert-Agfa N.V. in order to obtain direct-positive images with very steep gradation curve. By a "lith" developer there is understood a developing composition for light-exposed silver halide containing a hydrogen sulphite-addition compound of an aliphatic aldehyde or ketone e.g. formaldehyde hydrogen sulphite, and hydroquinone as the sole developing agent.

The following examples illustrate the present invention.

EXAMPLE 1

75 ml. of a 3 N aqueous solution of potassium bromide and 75 ml. of a 3 N aqueous solution of silver nitrate were introduced simultaneously at a rate of 10 ml. per minute into a precipitation flask containing 650 ml. of a 4% by weight aqueous gelatin solution to which at 50° C. an aqueous solution of ammonia was added in order to obtain a pH value of 9.3. During precipitation of the silver bromide the pAg-value was adjusted to and maintained at a value corresponding to an E.M.F. of +20 m.v (Ag/saturated reference calomel electrode).

Subsequently, the internal ripening was effected. For that purpose 3.5 ml. of a 10^{-2} molar solution of formamidine sulphinic acid were added and the emulsion digested for 30 minutes at 50° C. Then the pH was lowered to 6.5 and 1.5 ml. of an aqueous 0.08% by weight solution of gold(III)chloride and 1.5 ml. of aqueous 2% by weight solution of ammonium thiocyanate were added. After said addition the digestion was continued for 10 minutes at 50° C.

The precipitation was then continued (second precipitation) as follows: an aqueous solution of ammonia was added to obtain a pH value of 9.3 whereupon 665 ml. of an aqueous 3 N potassium bromide solution and 665 ml. of an aqueous 3 N silver nitrate solution were introduced at a rate of 19 ml. per minute. During precipitation the pAg value was maintained at a value corresponding to an E.M.F. of +20 mv. (Ag/saturated calomel electrode). The emulsion was solidified after the addition of 234 g. of gelatin and washed in the usual way.

After washing, the pAg was again adjusted to a value corresponding to an E.M.F. of +20 mv. (Ag/saturated calomel electrode) and the pH of the emulsion was adjusted to 6.5.

The external fogging of the composite silver bromide granules formed was then carried out for 80 minutes at 55° C. with 9 ml. of a 10^{-2} molar aqueous solution of formamidine sulphinic acid per kg. emulsion, containing 110 g. of silver bromide and 80 g. of gelatin.

After the fogging treatment, the emulsion was divided into several aliquot portions. The emulsion portions were cooled to 35° C. and the sensitizers listed in the table below were added in the amount given. The emulsion portions were kept for 30 min. at 35° C. whereupon per kg. 1 g. of saponin was added as coating aid. Just before coating 500 mg. of formaldehyde were added per kg. for hardening purposes. The various emulsion samples were then coated on a polyethylene terephthalate resin support and dried.

The materials formed were exposed to incandescent bulb light through a grey test wedge and developed for 135 sec. at 20° C. in a "lith"-type developing bath A of the following composition:

	G.
Hydroquinone	13
Formaldehyde hydrogen sulphite	50
Anhydrous sodium carbonate	60
Potassium bromide	1.5
The oxyethylene units containing polycondensation product prepared as described in preparation 2 of U.K. patent specification 920,637 filed May 7, 1959 by Gevaert Photo-Producten N.V.	0.5
Water to make 1000 ml.	

and in a developing bath B having the following composition:

Water (40° C.)	ml	800
p-Monomethylaminophenol sulphate	g	1.5
Anhydrous sodium sulphite	g	25
Hydroquinone	g	6
Anhydrous sodium carbonate	g	40
Potassium bromide	g	1
Water to make 1000 ml.		

The sensitometric results obtained are listed in Tables I (developing bath A) and II (developing bath B) hereinafter.

In these tables the total speed (S) is expressed on a percentage basis with respect to a reference emulsion, which comprises no sensitizing dye and for which arbitrarily a total speed of 100 is given.

The density in the exposed areas (minimum density) is a measure of the brightness of the whites and is denoted in the tables by D_{min}.

In the tables are also given the maximum density (D_{max}) obtained as well as the silver bromide content per sq. m. of the materials examined.

TABLE I

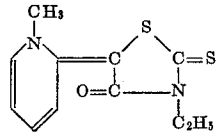
Sensitizer(s) per kg. of emulsion	D_{min}	D_{max}	Gamma	S	G. AgBr/ sq. m.
None	0.01	3.54	5.30	100	6.83
200 mg. of dye 1	0.01	3.88	3.90	536	7.96
200 mg. of dye 2	0.06	3.80	4.70	186	7.51
200 mg. of dye 3	0.01	4.06	9.00	257	7.83
100 mg. of dye 1 plus 100 mg. of dye 2	0.03	3.46	4.60	4,360	7.01
100 mg. of dye 1 plus 100 mg. of dye 3	0.01	3.82	7.30	2,690	7.71

TABLE II

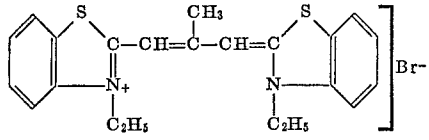
Sensitizer(s) per kg. of emulsion	D_{min}	D_{max}	Gamma	S	G. AgBr/ sq. m.
None	0.01	3.42	5.10	100	6.83
200 mg of dye 1	0.01	3.84	4.10	563	7.96
200 mg. of dye 2	0.06	3.78	4.30	159	7.51
200 mg. of dye 3	0.01	3.90	5.10	100	7.83
100 mg. of dye 1 plus 100 mg. of dye 2	0.03	3.54	4.60	4,080	7.01
100 mg. of dye 1 plus 100 mg. of dye 3	0.01	3.90	7.30	2,630	7.71

The dyes used in the above tables have the following structural formulae:

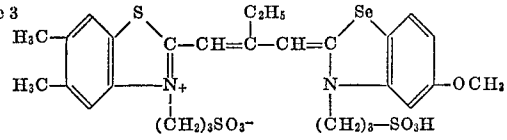
Dye 1



Dye 2



Dye 3



Example 2

Example 1 was repeated with the difference that development took place in developing bath B and the following carbocyanine dye was used.

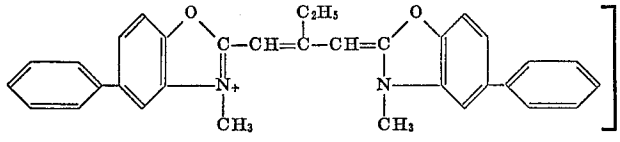


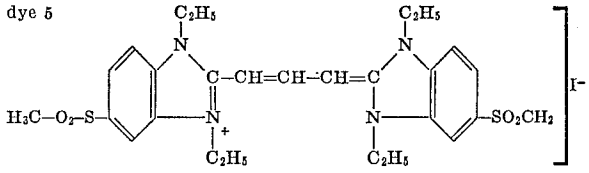
TABLE III

Sensitizers per kg. of emulsion	D_{min}	D_{max}	Gamma	Speed	G. AgBr/ sq. m.
None	0.01	3.18	5.15	100	6.61
200 mg. of dye 1	0.01	3.60	4.65	590	7.22
200 mg. of dye 4	0.04	3.64	3.60	563	7.65
100 mg. of dye 1 plus 100 mg. of dye 4	0.01	3.88	5.45	1,590	8.17

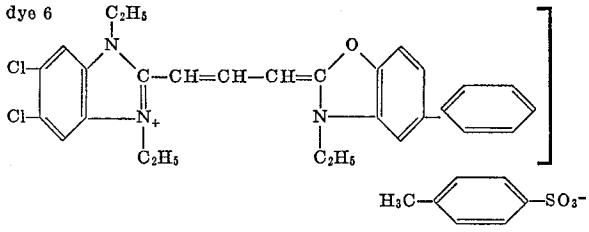
EXAMPLE 3

Exaample 1 was repeated with the difference that the following carbocyanine dyes were used.

dye 5



dye 6



The results obtained after development in developing baths A and B of Example 1 are listed in the Tables IV (bath A) and V (bath B) below.

TABLE IV

Sensitizers per kg. of emulsion	D_{min}	D_{max}	Gamma	Speed	G. AgBr/ sq. m.
None	0.01	4.14	4.70	100	7.90
200 mg. of dye 1	0.01	3.76	4.20	660	6.95
200 mg. of dye 5	0.01	4.34	5.90	95	7.48
200 mg. of dye 6	0.01	4.24	4.70	417	8.06
100 mg. of dye 1 plus 100 mg. of dye 5	0.01	4.36	4.30	1,450	7.66
100 mg. of dye 1 plus 100 mg. of dye 6	0.01	4.02	4.60	1,020	7.87

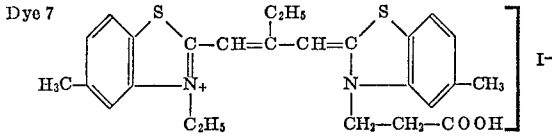
TABLE V

Sensitizers per kg. of emulsion	D_{min}	D_{mix}	Gamma	Speed	G. AgBr/ sq. m.
None	0.01	4.14	5.10	100	7.90
200 mg. of dye 1	0.01	3.60	4.60	795	6.95
200 mg. of dye 5	0.01	3.75	4.60	170	7.48
200 mg. of dye 6	0.01	4.42	4.40	340	8.06
100 mg. of dye 1 plus 100 mg. of dye 5	0.01	4.08	4.60	1,660	7.66
100 mg. of dye 1 plus 100 mg. of dye 6	0.01	4.36	4.95	1,175	7.87

EXAMPLE 4

Example 1 was repeated with the difference that the following carbocyanine dye was used

Dye 7



The results obtained after development in developing baths A and B of Example 1 are listed in Tables VI (bath A) and VII (bath B) below.

TABLE VI

Sensitizer(s) per kg. of emulsion	D_{min}	D_{max}	Gamma	Speed	G. AgBr/ sq. m.
None	0.01	3.46	9.10	100	6.13
200 mg. of dye 1	0.01	3.86	4.53	500	7.35
200 mg. of dye 7	0.05	4.26	5.20	550	7.61
100 mg. of dye 1 plus 100 mg. of dye 7	0.02	3.74	5.67	2,240	6.81

TABLE VII

Sesitizers kg. of emulsion	D_{min}	D_{max}	Gamma	Speed	G.AgBr/ sq.m.
None	0.01	3.34	7.15	100	6.13
200 mg. of dye 1	0.01	3.88	4.45	780	7.35
200 mg. of dye 7	0.05	4.14	5.13	400	7.61
100 mg. of dye 1 plus 100 mg. of dye 7	0.02	3.76	5.40	3,390	6.81

Example 5

Emulsions were prepared as described in Example 1 to which the ingredients listed in the table below were added in the amounts given. The various emulsion samples were coated on a baryta-coated paper support and dried.

The values of maximum and minimum density and of the speed obtained after conventional black-and-white processing and colour processing are listed in the Table VIII below. For the speed, the increase in log exposure values is given with reference to the emulsion to which no compound was added. An increase of the value by +0.3 means a doubling of the speed.

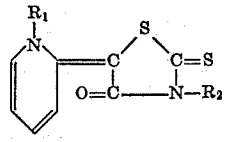
TABLE VIII

Compounds added per kg. emulsion	Black-and-white processing D_{min}	D_{max}	Speed (Δ log It)	Colour processing D_{min}	D_{max}	Speed (Δ log It)
None	0.11	1.32	Reference			
24 g. of N-n-hexadecyl-1-hydroxy-4-chloro-2-naphthamide as colour coupler	0.12	1.35	+0.1	0.15	1.60	Reference
200 mg. of dye 3	0.11	1.30	+0.6			
200 mg. of dye 3 plus 24 g. of the above colour coupler	0.13	1.35	+0.9	0.16	1.63	+1.05
200 mg. of dye 3 plus 100 mg. of dye 1	0.11	1.34	+1.95			
200 mg. of dye 3 plus 100 mg. of dye 1 plus 24 g. of the above colour coupler	0.11	1.38	+2.25	0.15	1.58	+2.55

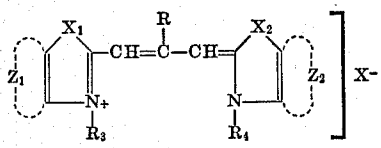
What we claim is:

1. A direct-positive photographic silver halide emulsion, which comprises silver halide grains having a central core of silver halide containing centres promoting the deposition of photolytic silver and over said core and outer shell of silver halide, which has been fogged, wherein said outer shell comprises adsorbed thereto a 2-pyridine-rhodanine merocyanine dye corresponding to the following general Formula I and a carbocyanine dye corresponding to the following General Formula II:

I.



II.



wherein:

R_1, R_2, R_3, and R_4 stand for a saturated or unsaturated aliphatic group, a cycloaliphatic group or an aryl group,

X_1 and X_2 stand for oxygen, sulphur, selenium, or the group $N(R_5)$, wherein R_5 has the same significance as given for R_1–R_4,

Z_1 and Z_2 stand for the atoms necessary to close a fused-on aromatic nucleus of the benzene series,

R stands for hydrogen, or lower alkyl, and

X stands for an anion but does not exist when one of R_3, R_4, and R_5 itself contains an anionic group.

2. A direct-positive emulsion according to claim 1, wherein the dyes are each present at a concentration of 50 mg. to 500 mg. per mole of silver halide.

3. A direct-positive emulsion according to claim 1, wherein the said centres are formed by chemical sensitization of the interior core of silver halide.

4. A direct-positive emulsion according to claim 1, wherein said centres are formed by reduction sensitization of the interior core of silver halide or treatment with a noble metal compound or by the said reduction sensitization together with said treatment with a noble metal compound.

5. A direct-positive emulsion according to claim 4, wherein reduction sensitization occurs by treatment with a reduction sensitizer.

6. A direct-positive emulsion according to claim 4, wherein reduction sensitization occurs by digestion of the cores at low pAg values.

7. A direct-positive emulsion according to claim 4, wherein said noble metal compound is a gold compound.

8. A direct-positive emulsion according to claim 1, wherein fogging of the outer shell of silver halide is effected by treatment with a reduction sensitizer or gold sensitizer or with both sensitizers together.

9. A direct-positive emulsion according to claim 4, wherein the reduction sensitizer used in the chemical sensitization of the silver halide core is the same as the reduction sensitizer used for fogging the silver halide emulsion.

10. A direct-positive emulsion according to claim 9, wherein said reduction sensitizer is thiourea dioxide.

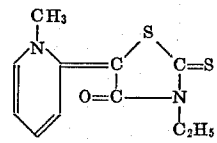
11. A direct-positive emulsion according to claim 1, wherein the silver halide of the interior core as well as the silver halide of the outer shell is silver bromide.

12. A direct-positive emulsion according to claim 1, wherein at least 95% by weight of said grains have a diameter, which is within about 40% of the mean grain diameter.

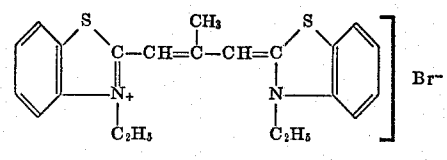
13. A direct-positive emulsion according to claim 1, which comprises a colour coupler.

14. A direct-positive photographic element, which comprises a support and at least one layer of an emulsion according to claim 1.

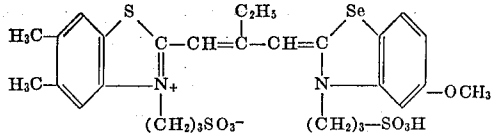
15. A direct-positive emulsion according to claim 2 wherein the dye of Formula I is



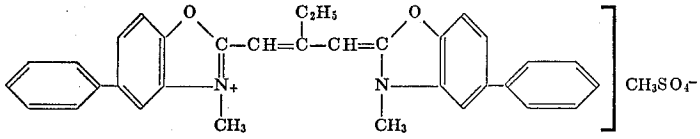
16. A direct-positive emulsion according to claim 15 wherein the dye of Formula II is



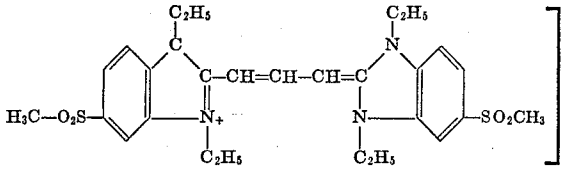
17. A direct-positive emulsion according to claim 15 wherein the dye of Formula II is



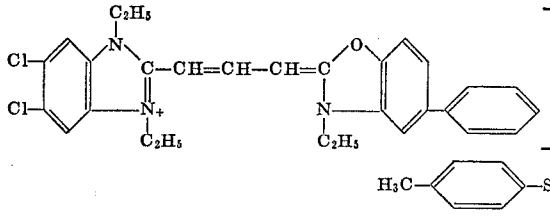
18. A direct-positive emulsion according to claim 15 wherein the dye of Formula II is



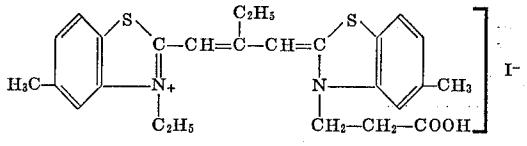
19. A direct-positive emulsion according to claim 15 wherein the dye of Formula II is



20. A direct-positive emulsion according to claim 15 wherein the dye of Formula II is



21. A direct-positive emulsion according to claim 15 wherein the dye of Formula II is



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U.S. Cl. X.R.

96—64, 100, 107, 108