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INFRARED-SENSITIZED SILVER HALIDE SYSTEMS

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ABSTRACT OF THE DISCLOSURE

This invention relates to improved infrared-sensitization of silver halide emulsions containing silver halide grains having metal dopants occluded therein. In one aspect, methine dyes having a primary radiation-adsorption peak above 700 nanometers can be used in combination with silver halide emulsions containing grains having metal dopants occluded therein to produce highly improved infrared sensitivity. In another aspect, infrared-absorbing dyes can be used in combination with the silver halide emulsions of this invention in high concentrations which would normally cause considerable desensitization of a surface-sensitive silver halide emulsion.

This invention relates to improved silver halide emulsions sensitized with infrared sensitizers. In one aspect, this invention relates to internal-image, silver halide emulsions comprising unfogged, silver halide grains which contain chemically formed internal sensitivity sites and wherein said grains have adsorbed to the surface thereof an infrared-sensitizing dye. In another aspect, this invention relates to an improved process for making negative-image records from infrared exposures.

It is known in the prior art that silver halide emulsions can be sensitized to the infrared portion of the electromagnetic spectrum. However, many of the dyes used to obtain sensitivity in the infrared portion of the spectrum produce loss of blue-speed sensitivity. Thus, the efficiency of the system is substantially lowered whereby extremely long exposures are necessary for recording infrared exposures. Therefore, improved photographic systems are desirable for recording infrared exposures.

We have now found that infrared-absorbing dyes can be used effectively in combination with certain internal-image silver halide emulsions to provide improved speed, efficiency and improved photographic properties. The preferred internal-image silver halide emulsions used in the improved combination of this invention contain unfogged silver halide grains which contain chemically treated sites for the deposition of photolytic or latent image silver internal to the grains, preferably formed by occluding polyvalent metal ions inside the grain.

In one embodiment, this invention relates to infrared-sensitized silver halide emulsion systems with improved photographic properties.

Another embodiment of this invention relates to internal-image emulsions containing polymethine infrared-absorbing dyes.

In a highly preferred embodiment of this invention, the silver halide emulsions comprise organic infrared-sensitizing dyes which have their primary absorption peak in the infrared region of the spectrum wherein said dyes are dicarbocyanines, tricarbocyanines, tetracarbocyanines, pentacarbocyanines, merocyanines, merodicarbocyanines, merotricarbocyanines, polynuclear merocyanines, complex merocyanines and the like.

In another highly preferred embodiment, the internal-image emulsions of this invention comprise unfogged silver halide grains which are chemically sensitized internally and wherein said emulsion comprises an infrared-absorbing dye in a concentration sufficient to cover at least 50% of the total available surface of the silver halide grains and preferably at least 70% of the total available surface.

In another embodiment, the infrared-sensitizing dyes are used in a concentration above that which would produce a loss in blue sensitivity in a sulfur and gold surface-sensitized silver bromoiodide emulsion (6 mole percent iodide) of at least 0.3 log E when developed in a surface developer such as Kodak D-19.

The term "internal-image emulsion" as used herein refers to those emulsions wherein a predominant amount of the blue sensitivity is internal to the grains of said emulsion. Such internal-image emulsions are those which, when tested according to normal photographic testing techniques by coating a test portion of the emulsion on a transparent support, exposing to a light-intensity scale for a fixed time between 1×10^{-6} and 1 second, bleaching 5 minutes in a 0.3% potassium ferricyanide solution at 65° F. and developing for about 5 minutes at 65° F. in Developer B below (an "internal-type" developer), have a sensitivity, measured at a density of 0.1 above fog, greater than the sensitivity of an identical test portion which has been exposed in the same way and developed for 6 minutes at 68° F. in Developer A below (a "surface-type" developer). Generally, the internal-image radiation emulsions have a predominant amount of sensitivity internal to the grain and preferably have a ratio of total sensitivity to surface sensitivity of greater than 10. Developer A is the usual type of surface-image developer and Developer B is an internal developer having high silver halide solvent activity.

Developer A:	G.
N-methyl-p-aminophenol sulfate	2.5
Ascorbic acid	10.0
Potassium metaborate	35.0
Potassium bromide	1.0
Water to make 1 liter.	
pH of 9.6.	

Developer B:	
N-methyl-p-aminophenol sulfate	2.0
Sodium sulfite, desiccated	90.0
Hydroquinone	8.0
Sodium carbonate, monohydrate	52.5
Potassium bromide	5.0
Sodium thiosulfate	10.0
Water to make 1 liter.	

The internal-image emulsions which are useful according to this invention are those which contain grains having a metal dopant occluded therein. The metal dopants can be occluded within the grain, for example, by precipitating in the presences of foreign ions (i.e., other than silver ions); by chemically sensitizing a core of a silver halide grain to form a metal or metal salt thereon and then forming a shell or outer region on the core occluding the chemically sensitized site within the grain; etc. Typical useful silver halide emulsions containing grains having metal dopants occluded therein can be prepared by the procedures disclosed in Porter et al., U.S. Pat. 3,206,-313 issued Sept. 14, 1965; Porter et al., U.S. Pat. 3,317,-322 issued May 2, 1967; Berriman, U.S. Pat. 3,367,778 issued Feb. 6, 1968, omitting the surface fogging procedure; British Pat. 1,027,146; Bacon et al., U.S. Pat. 3,447,927 issued June 3, 1969; Bacon et al., U.S. Ser. No. 629,090 filed Apr. 7, 1967; Berriman, British Pat. 1,151,782; McBride, U.S. Pat. 3,271,157 issued Sept. 6, 1966; and the like.

The silver halides used in the present invention are unfogged or at least they are bleached before chemical de-

velopment to provide an unfogged emulsion. Such silver halide emulsions contain no visible or substantial developable surface latent image.

The silver halide emulsions may be coarse- or fine-grain emulsions and can be prepared by many of the procedures available for making silver halide emulsions, e.g., single-jet emulsion procedures, double-jet emulsion procedures, ammonical emulsions, thiocyanate and/or thioether ripened emulsions, emulsions prepared using increased flow rates as disclosed in U.S. Ser. No. 11,838 by Wilgus filed Feb. 16, 1970, hot nucleation procedures as disclosed in U.S. Ser. No. 31,351 by Musliner filed Apr. 23, 1970, and the like.

In a preferred embodiment, the silver halide grains are formed in the presence of foreign metal ions, i.e., metal ions exclusive of silver, and preferably polyvalent metal ions. Generally, when the grains are formed in an aqueous medium, the silver halide grains are formed in the presence of the water-soluble salts of the respective metal, preferably in an acidic medium. Typical useful polyvalent metal ions include trivalent metal ions such as antimony, bismuth, arsenic, gold, iridium, rhodium and the like and tetravalent metal ions such as platinum, osmium, iridium and the like. In highly preferred embodiments, the grains are formed in the presence of bismuth, lead, iridium or osmium ions. Generally, the silver halide grains contain at least about 10^{-9} and preferably at least 10^{-3} mole percent dopant based on silver halide.

The internal-image emulsions can also be formed by other methods which will yield a metal dopant occluded within the grain. It is understood, of course, that the term "metal dopant" refers to any metal, metal ion or metal-containing compound which disrupts or changes the orderly silver ion-halide ion lattice in the silver halide grain or crystal. Therefore, the metal dopants useful according to this invention include such compounds as silver sulfide, silver telluride, silver selenide, mtallic silver, metallic gold, selenium, tellerium, gold sulfide and the like. Generally, any of the methods which are useful to produce centers which promote the deposition of photolytic silver can be used to provide the metal dopants within the silver halide grain. However, preferred metal dopants occluded within the grain contain at least one metal or metal ion other than silver (i.e., a foreign metal atom) and, in certain highly preferred embodiments, the metal of the metal dopant is a trivalent or tetravalent metal ion.

It is believed that the unexpected improvements in photographic properties obtained with the combination of the internal-image emulsions comprising grains having metal dopants therein and the infrared-sensitizing dyes are obtained because the metal dopants provide stronger electron traps than the infrared dyes which can also act as electron traps. However, applicants offer this theory only as a possible explanation for the improved results and do not want to be bound entirely by this theory.

The silver halide grains of this invention can additionally be surface-sensitized as long as they contain a strong metal dopant occluded therein, such as a trivalent or tetravalent metal ion or the equivalent thereof. Typical useful techniques for surface-sensitizing an imulsion are disclosed in Porter et al., U.S. Patent 3,317,322 issued May 2, 1967.

The infrared-absorbing dyes are utilized in combination with the doped emulsions of this invention in concentrations of generally above 100 mg./per mole of silver halide. However, in certain preferred embodiments, the dyes are used in a concentration above that which would produce a loss in blue sensitivity in a sulfur and gold surface-sensitized, silver bromoiodide emulsion (6 mole percent iodide) of at least 0.3 log E when developed in a surface developer such as Kodak D–19.

The infrared-sensitizing dyes which are especially useful according to this invention are those which have a primary absorption peak at a wave length of above 700 millimicrons and preferably above 800 millimicrons. Typical dyes which produce improved photographic properties, such as improved sensitivity, when used in combination with the internal-image emulsions of this invention include:

1,1′-diethyl-4,4′-tricarbocyanine iodide neocyanine
3,3′-diethylthiatricarbocyanine iodide
12-acetoxy-3,3′-diethylthiatetracarbocyanine perchlorate
12-acetoxy-3,3′-diethylthiapentacarbocyanine perchlorate
3,3′-diethyl-9,11-neopentylenethiatetracarbocyanine iodide
3,3′-diethyl-9,11; 15,17-dineopentylenethiapentacarbocyanine iodide

Generally, the infrared-absorbing polycarbocyanines disclosed on pp. 882–901 of Glafkides, Photographic Chemistry, vol. 2, 1960, Fountain Press, London, can be used effectively in combination with the emulsions disclosed above which contain metal dopants occluded in the grains. Other useful dyes which can be used in the emulsion combinations of this invention include the infrared-absorbing dyes disclosed in U.S. Patents No. 2,734,900 and No. 2,756,227; the enamines disclosed in Fumia et al., U.S. Patent 3,482,978; the enamines as disclosed in Hiller, U.S. Ser. No. 860,394 filed Sept. 23, 1969, now abandoned and the like.

The silver halide emulsions of this invention can be protected against the production of fog and can be stabilized against loss of sensitivity during keeping. Suitable antifoggants and stabilizers each used alone or in combination include thiazolium salts described in U.S. Patents 2,131,038 by Brooker et al. and 2,694,716 by Allen et al.; the azaindenes described in U.S. Patents 2,886,437 by Piper and 2,444,605 by Heimbach et al.; the mercury salts as described in U.S. Patent 2,728,663 by Allen et al.; the urazoles described in U.S. Patent 3,287,135 by Anderson et al.; the sulfocatechols described in U.S. Patent 3,236,652 by Kennard et al.; the oximes described in British Patent 623,448 by Carroll et al.; nitron; nitroindazoles; the mercaptotetrazoles described in U.S. Patents 2,403,927 by Kendall et al., 3,266,897 by Kennard et al. and 3,397,987 by Luckey et al.; the polyvalent metal salts described in U.S. Patent 2,839,405 by Jones; the thiuronium salts described in U.S. Patent 3,220,839 by Herz et al.; and the palladium, platinum and gold salts described in U.S. Patents 2,566,263 by Trivelli et al. and 2,597,915 by Yutzy et al.

The photographic elements of this invention may contain incorporated developing agents such as hydroquinones, catechols, aminophenols, 3-pyrazolidones, ascorbic acid and its derivatives, reductones and phenylenediamines. Combinations of developing agents can be employed in the practice of the invention. The developing agents can be in a silver halide emulsion and/or in another suitable location in the photographic element. The developing agents may be added from suitable solvents or in the form of dispersions as described in Yackel, U.S. Patent 2,592,-368, and Dunn et al., French Patent 1,505,778.

The photographic and other hardenable layers used in the practice of this invention can be hardened by various organic or inorganic hardeners, alone or in combination, such as the aldehydes, and blocked aldehydes, ketones, carboxylic and carbonic acid derivatives, sulfonate esters, sulfonyl halides and vinyl sulfonyl ethers, active halogen compounds, epoxy compounds, aziridines, active olefins, isocyanates, carbodiimides, mixed-function hardeners and polymeric hardeners such as oxidized polysaccharides like dialdehyde starch and oxyguargum and the like.

The photographic emulsions and elements described in the practice of this invention can contain various colloids alone or in combination as vehicles, binding agents and various layers. Suitable hydrophilic materials include both naturally occurring substances such as proteins, for example, gelatin, gelatin derivatives, cellulose derivatives, polysacchardies such as dextran, gum arabic and the like; and

synthetic polymeric substances such as water-soluble polyvinyl compounds like poly(vinylpyrrolidone), acrylamide polymers and the like.

The described photographic emulsion layers and other layers of a photographic element employed in the practice of this invention can also contain, alone or in combination with hydrophilic, water-permeable colloids, other synthetic polymeric compounds such as dispersed vinyl compounds such as in latex form and particularly those which increase the dimensional stability of the photographic materials. Suitable synthetic polymers include those described, for example, in U.S. Patents 3,142,568 by Nottorf issued July 28, 1964; 3,193,386 by White issued July 6, 1965; 3,062,674 by Houck et al. issued Nov. 6, 1962; 3,220,844 by Houck et al. issued Nov. 30, 1965; 3,287,289 by Ream et al. issued Nov. 22, 1966; and 3,411,911 by Dykstra issued Nov. 19, 1968; particularly effective are those water-insoluble polymers or latex copolymers of alkyl acrylates and methacrylates, acrylic acid, sulfoalkyl acrylates or methacrylates, those which have cross-linking sites which facilitate hardening or curing, those having recurring sulfobetaine units as described in Canadian Patent 774,054 by Dykstra, and those described in U.S. Patent 3,488,708 by Smith issued Jan. 6, 1970.

The photographic layers and other layers of a photographic element employed and described herein can be coated on a wide variety of supports. Typical supports include cellulose nitrate film, cellulose ester film, poly(vinyl acetal) film, polystyrene film, poly(ethylene terephthalate) film, polycarbonate film and related films or resinous materials, as well as glass, paper, metal and the like. Typically, a flexible support is employed, especially a paper support, which can be partially acetylated or coated with baryta and/or an alpha-olefin polymer, particularly a polymer of an alpha-olefin containing 2 to 10 carbon atoms such as polyethylene, polypropylene, ethyleneebutene copolymers and the like.

This invention may be used with elements designed for colloid transfer processes such as described in U.S. Patent 2,716,059 by Yutzy et al.; silver salt diffusion transfer processes such as described in U.S. Patents 2,352,014 by Rott, 2,543,181 by Land, 3,020,155 by Yackel et al. and 2,861,885 by Land; color image transfer processes such as described in U.S. Patents 3,087,817, 3,185,567 and 2,983,606 by Rogers, 3,253,915 by Weyerts et al., 3,227,550 by Whitmore et al., 3,227,551 by Barr et al., 3,227,552 by Whitmore and 3,415,644, 3,415,645 and 3,415,646 by Land; and imbibition transfer processes as described in U.S. Patent 2,882,156 by Minsk.

This invention may be used with elements designed for color photography, for example, elements containing color-forming couplers such as those described in U.S. Patents 2,376,679 by Frohlich et al., 2,322,027 by Jelley et al., 2,801,171 by Fierke et al., 2,698, 794 by Godowsky, 3,227,554 by Barr et al. and 3,046,129 by Graham et al.; or elements to be developed in solutions containing color-forming couplers such as those described in U.S. Patents 2,252,718 by Mannes et al., 2,592,243 by Carroll et al. and 2,950,970 by Schwan et al.; and in false-sensitized color materials such as those described in U.S. Patent 2,763,549 by Hanson.

Photographic elements prepared according to this invention can be processed by various methods which utilize internal-image silver halide developing compositions containing silver halide solvents and developing agents such as hydroquinones, catechols, aminophenols, 3-pyrazolidones, phenylenediamines, ascorbic acid derivatives, hydroxylamines, hydrazines, reductones and the like including procedures such as web processing as described in U.S. Patent 3,179,517 by Tregillus et al.; stabilization processing as described in Russell et al., "Stabilization Processing of Films and Papers," PSA Journal, vol. 16B, August 1950; monobath processing as described in Levy, "Combined Development and Fixation of Photographic Images With Monobaths," Phot. Sci, and Eng., vol. 2, No. 3, October 1958, and Barnes et al., U.S. Patent 3,392,019. If desired, the photographic elements of this invention can be processed in hardening developers such as those described in U.S. Patent 3,232,761 by Allen et al.; in roller transport processors such as those described in U.S. Patent 3,025,779 by Russell et al.; or by surface application processing as described in Example 3 of U.S. Patent 3,418,132 by Kitze.

The invention can be further illustrated by the following examples.

EXAMPLE 1–A

An iridium cored emulsion prepared as described by Berriman in U.S. Pat. 3,367,778, except without surface fogged grains, is used for the spectral-sensitizing experiments. The emulsion is prepared to the following specifications:

0.2μ cubic silver bromoiodide grains
2.3 kg. of emulsion/mole of silver
80.0 g. of gel/mole of silver pAg of 8.9

To 31 g. of the above emulsion are added 75 ml. of 5% gelatin, 1.0 ml. of a 7½% saponin solution and 0.5 ml. of a 10% formaldehyde solution.

To 10-ml. samples of the above emulsion mixture is added a 0.1% methanolic solution of the infrared-sensitizing dye 3,3'-diethyl-9,11; 15,17-dineopentylenethiapentacarbocyanine iodide. Sufficient 5% gelatin solution is added making a total of 15 ml. to yield coatings containing 0, 25, 50, 100, 200 and 400 mg. of dye per mole of silver.

Coatings .004" wet thickness are made on cellulose acetate subbed support. The dried coatings are exposed in a Bausch and Lomb spectrograph. Blue exposures are made at ½ sec. with a slit width of 1.0 mm. When the exposed strips are processed in an Elon-hydroquinone developer, no image is obtained until 1 g./l. of potassium iodide is added to cause the internal image to develop.

With the iodide-containing developer, all the coatings containing the infrared sensitizer produce the same blue speed. The lack of blue desensitization, even at high levels of this infrared sensitizer, is an indication of the powerful chemical sensitization provided by the iridium dopant. To observe the infrared response, a Corning CS2–59 is placed at the entrance slit of the spectrograph and exposures of 60 sec. at 10 mm. yield a good infrared response with a peak response at 1060 nm. after development in a solvent developer.

When similar coatings are made with the same type of emulsion, sulfur- plus gold-sensitized on the surface but without the iridium dopant, no detectable infrared response is observed under the same exposure conditions. The infrared response is still undetectable when the exposure time is increased to 5 minutes.

EXAMPLE 1–B

Further improvements in infrared speed can be obtained by hypersensitization of the coating just prior to exposure using a technique published by S. M. Solov'ev and N. M. Parfenova. Uspekhi Nauchi Fot., 7, 210 (1960).

The following technique is used to hypersensitize an infrared-sensitized coating containing silver halide grains having iridium ions occluded therein. A coating as described in Example 1–A is placed for 4 minutes in a solution of the following composition:

1.50 ml. of a 1.0% aqueous silver nitrate solution
0.75 ml. of a 28% aqueous ammonium hydroxide solution
distilled water to 100 ml.

The strip is rinsed in water for 1 minute, placed for 15 seconds in ethyl alcohol and then dried.

A good infrared response at 1060 nm. is then obtained

with a ½-second exposure at 1.0 mm. on the Bausch and Lomb spectrograph.

EXAMPLE 2

A variety of sensitizing dyes which range in sensitizing power from very good to strong desensitization in surface-sensitized emulsions are evaluated with the iridium cored emulsion.

To 31 g. of the emulsion described in Example 1–A are added 75 ml. of 5% gelatin, 1.0 ml. of a 7½% saponin solution and 0.5 ml. of a 10% formaldehyde solution. To 10 ml. of the above emulsion mixture is added the dye solution described in Example 1–A and a 5% gelatin solution to make a total of 15 ml. The mixture is held for 15 minutes at 40° C. and coated at .004" wet thickness on subbed cellulose acetate support.

After drying, the coatings are exposed in the wedge spectrograph for ½ second at 1.0 mm. with the following results:

Dye	Mg. dye/ mole Ag	Relative blue speed	Sensitized peak. nm.	Relative speed at peak
Control	0	160		
I	100	160	780	80
II	100	160	800	320
III	100	160	940	80
IV	200	160	740	320
V	100	160	840	640

NOTE.—The dyes are identified as follows: I=1,1'-diethyl-4-4'-carbocyanine iodide; II=1,1'-diethyl-2,2'-tricarbocyanine iodide; III=3,3'-diethyl-9,11-neopentylenethiatetracarbocyanine iodide; IV=3'3-diethylselenadicarbocyanine bromide; V=11-di(ethoxycarbonylmethyl) amino-3,3'-diethyl-10,12-ethylenethiatricarbocyanine iodide.

Similar results are obtained with a silver halide emulsion containing grains having osmium ions, bismuth ions or rhodium ions occluded therein and also with core-shell grain emulsions wherein the core has been sulfur- and gold-sensitized before forming the shell thereon.

EXAMPLE 3

Supersensitization of infrared response of iridium doped emulsions

The previous examples have demonstrated that the type of internal chemical sensitization provided by the iridium cored emulsion competes very effectively with any desensitizing material on the surface of the silver halide crystal so that desensitization no longer seems a problem with infrared spectral sensitization, but it is now possible further improvements in infrared spectral sensitization may result from an improvement in the transfer efficiency of spectral sensitization. This may be illustrated by the following:

Using the same emulsion as described in Example 2, a repeat coating is made using Dye III, 3,3'-diethyl-9,11-neopentylenethiatetracarbocyanine iodide, at a level of 100 mg. of dye/mole of silver. A second coating is made similar to the first coating described next above with the addition of 100 mg. of Calcofluor White (triazine-stilbene brightening agent manufactured by American Cyanamid Co.) added per mole of silver.

When these two coatings are given infrared exposures in a Bausch and Lomb spectrograph of ½ second at 1.0 mm., then developed in an Elon-hydroquinone developer containing 1 g./l. of potassium iodide, the coating containing both the infrared sensitizer and the Calcofluor White is faster than the control with dye alone by a factor of 4.

EXAMPLE 4

A radiation-sensitive gelatin silver chlorobromide photographic emulsion is prepared in the presence of bismuth ions as described in Example 18 of U.S. Pat. 3,447,927. The dyes are added to portions of the emulsion at the concentrations indicated (mg./Ag mole). All of the emulsion samples are coated with 34 g. of dithiourazole methyl vinyl ketone adduct as described in Wise et al., U.S. Ser. No. 816,867 filed Apr. 4, 1969 corresponding to U.S. Pat. 3,615,618, issued Oct. 26, 1971, and coated on a paper support at 60 mg. Ag/ft.^{2}.

Exposure

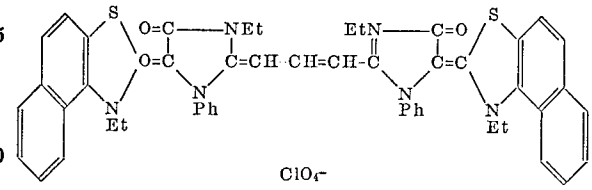
(1) 20" ¼ mm. slit width on Horton Spectrograph (this gives wave length scale=wedge spectrogram) (sensitizing maximum and range of sensitivity).

(2) ½" exposure on Eastman 1B sensitometer through no filters (Cl—clear speed), through Kodak Wratten 35+38A filters (B=blue speed) and through Wratten #16 filter (MB=minus blue speed) superimposed upon a 0.15 log *E* graded step wedge.

Samples of the coatings are heated on an aluminum block with a Teflon surface at a block temperature of 230° C., then photodeveloped for 5' under UV light. Speed is determined as the last step visible in the region of low exposure. Note that any B speel with an * is unreliable as the 35+38A filter transmits infrared radiation.

EXAMPLE 4–A

Dye VI—3,3'-diethyl-5,5'-bis(1-ethylnaphtho[1,2-d]thiozolin - 2-ylidene)-4,4'-dioxo-1,1'-diphenylimidazolinocarbocyanine perchlorate



Coatings are prepared with 0 and 400 mg. of Dye VI per mole of silver, exposed and processed as above, with 4 seconds' heating at 250° C.

Results:

Dye (mg./mole)	Cl	B	MB	$\lambda_{max.}$, nm.	λRange
Unsensitized	17	10	------	430	To 490 nm.
VI (400)	21	*10	19	730	To 800 nm.

EXAMPLE 4–B

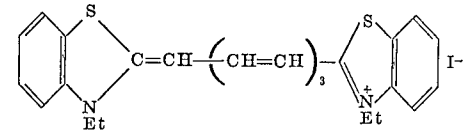
An emulsion is prepared according to Example 4 containing 3,3'-diethylsulfodicarbocyanine ethyl sulfate. The emulsion is exposed and developed with 5 seconds of heating at 230° C. as in Example 4 with the following results:

	Cl	B	MB	$\lambda_{max.}$, nm.	λRange
Control	13	6	------	430	To 490 nm.
Dye	16	12	15	780	520-840 nm.++.

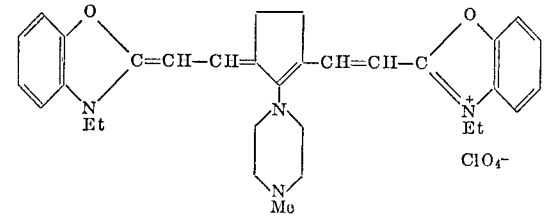
EXAMPLE–4–C

An emulsion is prepared as described in Example 4 containing Dyes VII and VIII.

Dye VII—3,3'-diethylthiatricarbocyanine iodide



Dye VIII—3,3'-diethyl-10,12-ethylene-1-(4-methyl-1-piperazinyl)oxatricarbocyanine perchlorate



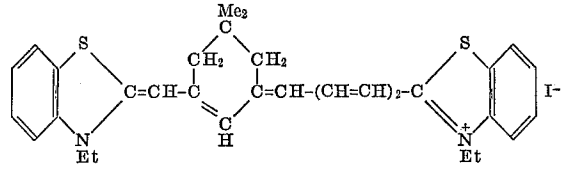
The emulsions are exposed and developed with 5 seconds of heating at 230° C. as in Example 4 with the following results:

Dye (mg./mole)	Cl	B	MB	λ_{max}, nm.	λRange
Unsensitized	13	6	------	430	To 480 nm.
VII (50)	16	*8	8	800	~600 to 850 nm.
VIII (400)	19	*11	17	740	480 to 840 nm.

EXAMPLE 4-D

An emulsion is prepared as lescribed in Example 4 containing Dye IX.

Dye IX—3,3'-diethyl-9,11-neopentylenethiatetracarbocyanine iodide



The emulsion, exposure and procesisng are as described in Example 4 with the exception that a sample of each coating is also exposed on an infrared sensitometer through an Interference Flter Set 15 Filter No. 1.0 (Optics Technology, Inc.).

Results:

Dye(mg./mole)	Cl	B	MB	Infrared speed
Unsensitized	14	6	--------	No speed.
IX (400)	15	*7	5	5 steps visible.

EXAMPLE 5

An internal-image emulsion, a bromoiodide emulsion (2.5 mole percent iodide) having an average grain size of 0.2 micron, is prepared by adding 106 mg. of potassium hexachloroiridate/mole of silver to the gelatin solution prior to the precipitation of the silver halide. The emulsion is divided into separate aliquot portions and to the portions are added 250, 500, 700 and 900 mg. of the infrared - sensitizing dye 3,3'-diethylthiatricarbocyanine iodide per silver mole. The emulsion samples are then coated on a film support at 100 mg. of silver/ft.^{2}. After exposing the coated samples on an Eastman 1B Sensitometer, the samples are developed in the internal-image developer of the following composition:

	G.
1-phenyl-3-pyrazolidone	10.0
Sodium isoascorbate	40.0
Sodium hydroxide	30.0
Sodium sulfite	20.0
1-phenyl-4-mercaptotetrazole	0.25
Potassium bromide	5.0
Potassium iodide	0.5
Distilled water to 1 liter.	

The results show no desensitization in the inherent sensitivity of the emulsion, and the best spectral response (800 nm.) is obtained at 900 mg. of dye-mole of silver.

EXAMPLE 6

An internal-image emulsion is prepared according to Example 5 with the following infrared dyes added to separate portions of the emulsions at the levels indicated in the following table. The samples are coated at 100 mg. of silver/ft.^{2}, and developed in the developer set forth in Example 5.

An internal-image emulsion, prepared and processed similar to that described in Example 5, is separated into equal portions and to the portions are added the infrared dyes at the levels described in the following table.

Infrared dye	Dye (mg./-Ag mole)	Spectral sensitivity
A	50	730
A	100	730
A	200	730
B	50	735
B	100	735
B	200	735
C	50	740
C	100	740
C	200	740
D	50	810
D	100	810
D	200	810

NOTE.—A=3-carboxymethyl-5-[4-(1-ethylnaphtho[1,2-d]thiazolin-2-ylidene)-2-butenylidene]rhodanine; B=1-carboxymethyl-5-[(3-ethyl-2(3H)-naphtho[2,1]-thiazolylidene)-2-butenylidene]-3-phenyl-2-thiohydantoin, pyridine salt; C=1,3-diethyl-5-[6-(3-ethyl-2(3)-benzothiazolylidene)hexadienylidene]barbituric acid; D=3-ethyl-5-[(2-ethyl-1(2)-benzothiazylidene)hexadienylidene]rhodanine.

In each instance the samples exhibit very high spectral sensitivity with little or no loss in blue-speed sensitivity.

EXAMPLE 7

An internal-image emulsion is prepared as described in Example 5. The emulsion is then chemically sensitized at the surface of the grains by adding 2.0 mg. of thiourea dioxide/silver mole and then finished to optimum. To the emulsion is added 500 mg. of the infrared-sensitizing dye 3,3'-diethylthiatricarbocyanine iodide per silver mole. After exposing and processing as described in Example 5, a 0.3 log *E* speed increase is noticed over an undyed control.

EXAMPLE 8

An internal-image emulsion is prepared with 900 mg. of the dye as described in Example 5. The emulsion is then coated at 100 mg. silver/ft.^{2} on a film support and exposed to 20 foot candles of illumination for 5 seconds through a line image. The coating is then rolled in contact with a receiver and pod with a viscous developer solution of the type described in U.S. Pat. 2,823,122. After 10 seconds, the receiver is separated from the film support and on the receiving layer is noticed a high-quality direct-positive image.

Although the invention has been described in considerable detail with particular reference to certain preferred embodiments thereof, variations and modifications can be effected within the spirit and scope of the invention.

We claim:

1. A photographic element comprising a support and at least one layer containing an internal-image silver halide emulsion comprising silver halide grains having metal dopants occluded therein and a concentration of an organic, sensitizing dye on the surface of said grain above the concentration which would produce a loss in blue sensitivity in a control sulfur and gold surface-sensitized silver bromoiodide emulsion, containing 6 mole percent iodide, of at least 0.3 log *E* when developed in Kodak Developer D-19 of the composition:

	G.
N-methyl-p-aminophenol sulfate	2.0
Sodium sulfite, desiccated	90.0
Hydroquinone	8.0
Sodium carbonate, monohydrated	52.2
Potassium bromide	5.0
Water to 1 liter.	

said dye having a radiation adsorption peak in the infrared region of the electromagnetic spectrum.

2. A photographic element according to claim 1 wherein said dye is a polymethine dye.

3. A photographic silver halide element according to claim 1 wherein said silver halide grains having "metal dopants" occluded therein are unfogged on the surface.

4. A photographic element according to claim 1 wherein said dye is a tricarbocyanine dye.

5. A photographic element according to claim 1 wherein said dye is a tetracarbocyanine dye.

6. A photographic element according to claim 1 wherein said dye is a pentacarbocyanine dye.

7. A photographic element according to claim 1 wherein said dye is a merocyanine dye.

8. A photographic element according to claim 1 wherein said dye is a dicarbomerocyanine dye.

9. A photographic element according to claim 1 wherein said metal dopants are metal ions.

10. A photographic element according to claim 1 wherein said metal dopants are trivalent metal ions.

11. A photographic element according to claim 1 wherein said silver halide grains contain iridium occluded therein.

12. A photographic element according to claim 1 wherein said dye is present in a concentration sufficient to cover at least 50% of the total available surface of said silver halide grains.

13. A photographic element according to claim 1 wherein said dye is present in a concentration sufficient to cover at least 70% of the total available surface of said silver halide grains.

14. A photographic element according to claim 1 wherein said silver halide grains are core-shell grains wherein the core has been sulfur- and gold-sensitized before forming a shell thereon.

15. A photographic element according to claim 1 wherein said dye is a carbocyanine dye.

16. A photographic element comprising a support and at least one layer containing a silver halide emulsion having a ratio of total sensitivity to surface sensitivity of greater than 10, comprising silver halide grains having metal dopants occluded therein and a concentration of an organic, sensitizing dye on the surface of said grains above the concentration which would produce a loss in blue sensitivity in a control sulfur and gold surface-sensitized silver bromoiodide emulsion, containing 6 mole percent iodide, of at least 0.3 log E when developed in Kodak Developer D–19 of the composition:

	G.
N-methyl-p-aminophenol sulfate	2.0
Sodium sulfite, desiccated	90.0
Hydroquinone	8.0

17. The photographic element according to claim 16 wherein said silver halide grains contain iridium occluded therein.

18. The photographic element according to claim 16 wherein said dye is a dicarbocyanine dye.

19. The photographic element according to claim 16 wherein said silver halide grains having metal dopants occluded therein are unfogged on the surface.

20. The photographic element according to claim 16 wherein said dye is present in a concentration sufficient to cover at least 50% of the total available surface of said silver halide grains.

21. The photographic element according to claim 16 wherein said dye is present in a concentration sufficient to cover at least 70% of the total available surface of said silver halide grains.

22. The photographic element according to claim 16 wherein said silver halide grains are core-shell grains wherein the core has been sulfur- and gold-sensitized before forming a shell thereon.

23. A photographic internal-image, silver halide emulsion comprising silver halide grains having metal dopants occluded therein and a concentration of an organic, sensitizing dye on the surface of said grains above the concentration which would produce a loss in blue sensitivity in a control sulfur and gold surface-sensitized silver bromoiodide emulsion, containing 6 mole percent iodide, of at least 0.3 log E when developed in Kodak Developer D–19 of the composition:

	G.
N-methyl-p-aminophenol sulfate	2.0
Sodium sulfite, desiccated	90.0
Hydroquinone	8.0
Sodium carbonate, monohydrated	52.5
Potassium bromide	5.0
Water to 1 liter.	

said dye having a radiation adsorption peak in the infrared region of the electromagnetic spectrum.

24. The photographic, internal-image, silver halide emulsion of claim 23 wherein said silver halide grains having metal dopants occluded therein are unfogged on the surface.

25. A photographic silver halide emulsion comprising silver halide grains having a ratio of total sensitivity to surface sensitivity of greater than 10 and having metal dopants occluded therein, and a concentration of an organic, sensitizing dye on the surface of said grains above the concentration which would produce a loss in blue sensitivity in a control sulfur and gold surface-sensitized silver bromoiodide emulsion, containing 6 mole percent iodide, of at least 0.3 log E when developed in Kodak Developer D–19 of the composition:

	G.
N-methyl-p-aminophenol sulfate	2.0
Sodium sulfite, desiccated	90.0
Hydroquinone	8.0
Sodium carbonate, monohydrated	52.5
Potassium bromide	5.0
Water to 1 liter.	

said dye having a radiation adsorption peak in the infrared region of the electromagnetic spectrum.

26. A photographic element comprising a support having thereon at least one layer containing an internal-image silver halide emulsion comprising silver halide grains, the surface of said grains being free of intentional chemical sensitization, said grains having occluded therein a metal dopant selected from the group consisting of antimony, bismuth, rhodium, platinum, osmium, iridium, and lead ions, and on the surface of said grains a concentration of organic, sensitizing dye having a radiation adsorption peak in the infra-red region of the electromagnetic spectrum, above that which would produce a loss in blue sensitivity in a control sulfur and gold surface-sensitized silver bromoiodide emulsion, containing 6 mole percent iodide, of at least 0.3 log E when developed in Kodak Developer D–19 having the composition:

	G.
N-methyl-p-aminophenol sulfate	2.0
Sodium sulfite, desiccated	90.0
Hydroquinone	8.0
Sodium carbonate, monohydrated	52.5
Potassium bromide	5.0
Water to 1 liter.	

References Cited

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NORMAN G. TORCHIN, Primary Examiner

R. E. FICHTER, Assistant Examiner

U.S. Cl. X.R.

96—64, 94, 107, 108, 101, 120, 132, 133; 250—65.1

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,690,891

DATED : September 12, 1972

INVENTOR(S) : J. Spence, P. B. Gilman, Jr., and C. G. Ulbing

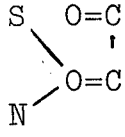
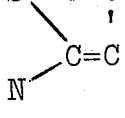
It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 55, "foreign ions" should read ---foreign metal ions---.

Column 3, line 37, "mtallic" should read ---metallic---; and, line 60, "imulsion" should read ---emulsion---.

Column 6, line 26, before "infrared" insert ---far---; and, line 60, "Nauchi" should read ---Nauch---.

Column 7, line 57, "Cyanamid" should read ---Cyanamide---.

Column 8, line 9, "Cl-clear" should read ---Cl=clear---; line 21, "thio" should read ---thia---; line 25, that part of formula reading "  " should read ---  ---; and,

line 64, "ethylene-l-" should read ---ethylene-ll- ---.

Column 9, line 11, "lescribed" should read ---described---; line 24, "procesisng" should read ---processing---; line 27, "Flter" should read ---Filter---; and, line 46, "/ft.^{2}." should read ---/ft^2.---.

Column 10, lines 70-71, " "metal dopants" " should read ---metal dopants---.

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,690,891

DATED : September 12, 1972

INVENTOR(S) : J. Spence, P. B. Gilman, Jr., and C. G. Ulbing

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

Column 11, line 43, insert

--- Sodium carbonate, monohydrated 52.5 g.
Potassium bromide 5.0 g.
Water to 1 liter

said dye having a radiation adsorption peak in the infrared region of the electromagnetic spectrum.---

Signed and Sealed this

twenty-ninth Day of June 1976

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks