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DIRECT-PRINT PHOTOGRAPHIC SILVER HALIDE EMULSIONS

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21 Claims. (Cl. 96—102)

ABSTRACT OF THE DISCLOSURE

Light-developable, direct-print silver halide emulsion containing halogen acceptors, sensitizing dyes and anti-unsensitizing compounds which enhance the sensitizing effect of the sensitizing dyes in the presence of the halogen acceptors.

The present invention relates to photography, and more particularly to light-developable, direct-print photographic silver halide emulsions.

Radiation-sensitive papers adapted for light recording, e.g., oscillographic recording, are well known. Typical of such papers are the developing-out and print-out type. The developing-out type, as the name implies, requires that the exposed material be chemically developed, fixed and washed in order to provide a useful visible image on said material. The print-out type of material develops on exposure and requires no development step. The print-out type is generally much slower than the developing-out type and the images are unstable and have a short life.

A third type of radiation-sensitive material especially suitable for "light-writing" and oscillographic recording comprises a silver halide emulsion layer which, when exposed to a high intensity source of light, forms a latent image which can then be developed by exposure to a second light source of lower intensity. Such direct-writing or direct-printing emulsions are faster than print-out emulsions and require no development. It is this latter type of emulsion that the present invention concerns.

A conventional high intensity light source used in oscillographic recording apparatus to expose photographic products having light-developable, direct-print silver halide emulsions coated thereon is a mercury vapor lamp. Mercury vapor lamps emit light that is rich in ultraviolet light. Silver halide emulsions are inherently sensitive to such light, and thus, there is no necessity to spectrally sensitize silver halide emulsions utilized with such light sources. However, the presence of mercury-containing apparatus is undesirable in confined areas such as in aircraft, submarines, ships and the like because of the toxic nature of mercury as well as its deleterious effect on such metals as aluminum.

Xenon lamps have been found to be particularly useful high intensity light sources for use in oscillographic recording apparatus as a replacement for mercury vapor lamps. Xenon light sources emit light having longer wavelengths than do mercury vapor light sources. Hence, it is desirable to spectrally sensitize silver halide emulsions utilized with apparatus having xenon light sources. However, many halogen acceptors that are utilized in light-developable, direct-print silver halide emulsions reduce the effectiveness of many conventional spectral sensitizing dyes by displacing or desorbing such dyes from the silver halide crystals of the emulsion.

It is an object of this invention to provide novel spectrally sensitized light-developable, direct-print silver halide emulsions.

It is another object of this invention to provide novel photographic silver halide emulsions suitable for preparing direct-print recording paper having a high rate of photodevelopment and high stability of the photodeveloped image.

It is another object of this invention to reduce the desorption of spectral sensitizing dyes from photographic silver halide grains caused by halogen acceptors by novel emulsion addenda.

It is another object of this invention to provide novel photographic light-developable, direct-print silver halide emulsions containing spectral sensitizing dyes that bleach on photodevelopment.

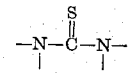
It is still another object of this invention to provide novel photographic light-developable, direct-print silver halide emulsions that can be chemically developed and fixed after photodevelopment to make archival-quality records.

It is likewise an object of this invention to provide new photodevelopable photographic silver halide emulsions that are characterized as having an improved density differential between the initially-exposed and unexposed areas upon photodevelopment.

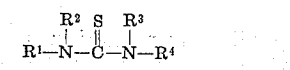
It is also an object of this invention to provide new photodevelopable photographic silver halide emulsions that have improved resistance in the initially-unexposed areas to density increase upon photodevelopment and subsequent exposure to light.

These and other objects of this invention are accomplished with spectrally sensitized light-developable, direct-print silver halide emulsions containing a thiourea halogen acceptor and a class of mercapto compounds that we have characterized as "anti-unsensitizers."

The halogen acceptors utilized in the photographic silver halide emulsions of the invention are thiourea compounds including thiourea itself and fully or partially substituted thioureas which include the thiourea grouping

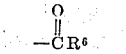


Typical suitable thiourea halogen acceptors have the structure



wherein:

R^1, R^2, R^3 and R^4 can be hydrogen atoms, alkyl radicals, aryl radicals such as those of the naphthyl and phenyl series, nitrogen-containing radicals such as amino radicals ($—NH_2$) and $—N{=}CH—R^5$ wherein R^5 is an alkyl or an aryl radical such as those of the naphthyl and phenyl series, acyl radicals



wherein R^6 is an alkyl or an aryl radical such as those of the naphthyl and phenyl series; and R^2 and R^3 can together be the necessary atoms to complete a heterocyclic nucleus with the thiourea grouping, the heterocyclic nucleus containing a carbon atom attached to at least one nitrogen atom, to form such cyclic compounds as an imidazolethione, an imidazolinethione, a triazinethiol, a thiobarbituric acid, a thiouracil or the like cyclic compounds and including such substituents as alkyl radicals and aryl radicals such as those of the naphthyl and phenyl series. The alkyl substituents in the described thioureas can be widely varied although alkyls having 1 to 18 carbon atoms are more generally used. The alkyl and aryl radicals of the described thioureas can be substituted or unsubstituted.

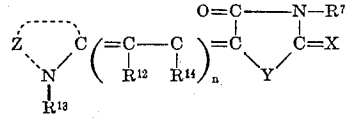
Illustrative thiourea halogen acceptors include:

1-methyl-2-imidazolethione

1-n-butyl-1,2,5,6-tetrahydro-1,3,5-triazine-4-thiol thiourea
1-methyl-2-imidazolinethione
1,3-dimethyl-2-imidazolinethione
2-imidazolinethione
thiosemicarbazide
tetramethylthiourea
D-mannose thiosemicarbazide
morpholino-2-propane thiosemicarbazide
D-galactose thiosemicarbazide
p-dimethylaminobenzoldehyde-thiosemicarbazone
1-isopentyl-2-thiourea
1-(2-diethylaminoethyl)-1,2,5,6-tetrahydro-1,3,5-triazine-4-thiol
1,2-bis(1,2,5,6-tetrahydro-1,3,5-triazine-4-thiol)ethane
1-phenyl-2-thiourea
1,3-diphenyl-2-thiourea
4-thiobarbituric acid
2-thiouracil
1-acetyl-2-thiourea
1,3-dibenzyl-2-thiourea
1,1-diphenyl-2-thiourea
1-ethyl-1-(α-naphthyl)-2-thiourea
2-imidazolethione
1-phenyl-2-imidazolinethione
4,5-diphenyl-2-imidazolinethione
1-(o-methoxyphenyl)-2-thiourea

The concentration of halogen acceptor utilized in the emulsions of the invention can be widely varied in accordance with usual practice. Generally, about .01 to 25 mole percent, and preferably about .1 to 5 mole percent, based on the silver halide in the emulsion is utilized.

Any of the conventional spectral sensitizing dyes can be utilized to spectrally sensitize the emulsions of the invention such as merocyanine dyes and cyanine dyes including carbocyanine, hemicyanine, styryl and the like dyes. Particularly useful spectral sensitizing dyes are merocyanine dyes having the formula



wherein:

X can be a sulfur or a selenium atom; R^7 can be an alkyl radical, an aryl radical such as phenyl, or a hydrogen atom; Y can be an oxygen atom, a sulfur atom, a selenium atom,



wherein R^{10} can be the same substituents as R^7, and



wherein R^{11} can be the same substituents as R^7; n is an integer of 0 to 2; R^{12} and R^{14} are hydrogen atoms, lower alkyl radicals or aryl radicals such as phenyl; R^{13} can be an alkyl radical or an aryl radical such as phenyl; and Z represents the non-metallic atoms required to complete a basic heterocyclic nucleus generally having 5 to 6 atoms in the heterocyclic ring such as carbon, sulfur, selenium, oxygen and nitrogen to form such moieties as a benzothiazole, a benzoxazole, a quinoline, a naphthothiazole, a naphthoxazole, a benzimidazole, a benzoselenazole, a naphthoselenazole, an oxazole, a thiazole, a thiazoline, a pseudoindole and the like. The Y substituent is preferably



to form a thiohydantoin nucleus. The alkyl substituents in the described merocyanine dyes can be widely varied although alkyls having 1 to 18 carbon atoms are more generally used, those alkyls denominated "lower" alkyls

having 1 to 4 carbon atoms. The alkyl and aryl radicals of the described dyes can be substituted or unsubstituted.

Typical suitable merocyanine dyes used to spectrally sensitize the emulsions of the invention include:

5-[(3-ethyl-2-benzothiazolinylidene)ethylidene)ethylidene]-rhodanine
5-[(3-ethyl-2-benzothiazolinylidene)ethylidene]-2-thio-2,4-oxazolidinedione
5-[(3-ethyl-2-benzothiazolinylidene)ethylidene]-3-heptyl-1-phenyl-2-thiohydantoin
5-[(1-ethylnaphtho{1,2-d}thiazolin-2-ylidene)ethylidene]-3-n-heptyl-1-phenyl-2-thiohydantoin
5-[(3-ethyl-2-benzothiazolinylidene)ethylidene]-2-thiohydantoin
5-[(3-ethylnaphth{2,1-d}oxazolin-2-ylidene)ethylidene]-3-n-heptyl-1-phenyl-2-thiohydantoin
5-[(3-ethyl-2-benzoxazolinylidene)ethylidene]-4-thiohydantoin
3-ethyl-5-[(3-ethyl-2-benzothiazolinylidene)ethylidene]-2-thiohydantoin
5-[di(3-ethyl-2-benzothiazolinylidene)isopropylidene]-1-methyl-2-thiobarbituric acid
5-[di(3-ethyl-2-benzothiazolinylidene)isopropylidene]-2-thiobarbituric acid
5-[4-(3-ethyl-2-benzothiazolinylidene)-2-butenylidene]-3-n-heptyl-1-phenyl-2-thiohydantoin
5-[(3-ethyl-5-phenyl-4-oxazolin-2-ylidene)ethylidene]-3-heptyl-1-phenyl-2-thiohydantoin
1-methyl-5-[(-1,3,3-trimethyl-2-indolinylidene)ethylidene]-2-thiobarbituric acid
5-[(3-ethyl-2-benzothiazolinylidene)ethylidene]-1-phenyl-2-thiobarbituric acid
5-[(3-ethylnaphth{2,1-d}oxazolin-2-ylidene)isopropylidene]-3-heptylrhodanine
1-ethyl-5-[(1-ethylnaphtho{1,2-d}thiazolin-2-ylidene)isopropylidene]-2-thiobarbituric acid
5-(3-ethyl-2-benzothiazolinylidene)-3-heptyl-1-phenyl-2-thiohydantoin
3-heptyl-5-(1-methylnaphtho{1,2-d}thiazolin-2-ylidene)-1-phenyl-2-thiohydantoin
5-[(1-ethyl-2-(1H)-quinolylidene)ethylidene]-3-lauryl-2-thio-2,4-oxazolidinedione
1-methyl-5-[(3-methyl-2-thiazolidinylidene)ethylidene]-2-thiobarbituric acid
5-[4-(3-methyl-2- benzoxazolinylidene)-1,3-neopentylene-2-butenylidene]-2-thiobarbituric acid
5-[(3-ethyl-2-benzoselenazolinylidene)ethylidene]-3-heptyl-2-thiohydantoin
5-[3-(1,2-dihydropyrrolo{2,1-d}benzothiazolyl)methylene]-3-heptyl-1-phenyl-2-thiohydantoin
5-[(5,6-dichloro-1,3-diethyl-2-benzimidazolinylidene)ethylidene]-1-ethyl-2-thiobarbituric acid
5-[(3-ethyl-2-benzothiazolinylidene)ethylidene]-3-heptyl-2-seleno-2,4-thiazolidinedione
5-[(3-ethyl-2-benzothiazolinylidene)ethylidene]-3-heptyl-2-thio-2,4-selenazolidinedione
5-[(3-ethyl-2-benzothiazolinylidene)ethylidene]-3-heptyl-rhodanine
5-[(3-ethyl-2-benzothiazolinylidene)ethylidene]-3-lauryl-rhodanine
5-[(3-ethyl-2-benzoxazolinylidene)ethylidene]-3-decyl-1-phenyl-2-thiohydantoin
5-[(3-ethyl-2-benzoxazolinylidene)ethylidene]-1-heptyl-3-phenyl-2-thiohydantoin

Other suitable dyes that can be utilized to optically sensitize the emulsions of the invention include:

3,3'-diethyl-9-methylthiacarbocyanine iodide
9-ethyl-3,3'-dimethyl-4,5,4',5'-dibenzothiacarbocyanine bromide
3,3',9-triethyl-5,5'-diphenyloxacarbocyanine iodide
9-ethyl-3,3'-di(β-methoxyethyl)-5,5'-diphenyloxacarbocyanine iodide

Typical suitable-sensitizing dyes are described in

Brooker U.S. Patents 1,846,301, issued Feb. 23, 1932; 1,846,302, issued Feb. 23, 1932; and 1,942,854, issued Jan. 9, 1934; White U.S. Patent 1,990,507, issued Feb. 12, 1935; Brooker and White U.S. Patents 2,112,140, issued Mar. 22, 1938; 2,165,338, issued July 11, 1939; 2,493,747, issued Jan. 10, 1950; and 2,739,964, issued Mar. 27, 1956; Brooker and Keyes U.S. Patent 2,493,748, issued Jan. 10, 1950; Sprague U.S. Patents 2,503,776, issued Apr. 11, 1950 and 2,519,001, issued Aug. 15, 1950; Heseltine and Brooker U.S. Patent 2,666,761, issued Jan. 19, 1954; Heseltine U.S. Patent 2,734,900, issued Feb. 14, 1956; Van Lare U.S. Patent 2,739,149, issued Mar. 20, 1956; British Patent 450,958, accepted July 15, 1936 and elsewhere in the literature.

The amount of sensitizing dyes utilized can be widely varied. The concentration of the dyes will vary according to the type of emulsion and according to the effect desired. The suitable and most economical concentration for any given emulsion will be apparent to those skilled in the art upon making the ordinary tests and observations customarily used in the art of emulsion making. Generally about 10 to 1000 mg. of dye per mole of silver halide in the emulsion are utilized. About .05 to 1 mole percent of sensitizing dye based on the silver halide in the emulsion is a typical working range. A single sensitizing dye or combinations of several sensitizing dyes can be used in the present emulsions for spectral sensitization.

At least one water-soluble halide in an amount sufficient to provide an excess of halide ions over that necessary initially to precipitate all of the silver as silver halide in the preparation thereof is desirably utilized. More generally, at least about .05 mole percent, and usually about .05 to 10 mole percent, of water-soluble halide based on the silver halide in the emulsion is utilized. Illustrative water-soluble halides include ammonium, calcium, lithium, magnesium, potassium, or sodium bromide, chloride or iodide. Water-soluble iodides are particularly useful.

Halogen acceptors, particularly of the sulfur-containing type, have a tendency to displace or desorb spectral sensitizing dyes from silver halide crystals and thus reduce or negate the sensitizing effect of the dye. In accordance with our invention, we utilize in our emulsions mercaptan anti-unsensitizers that enhance the sensitizing effect of spectral sensitizing dyes in the presence of thiourea halogen acceptors. Suitable mercaptan anti-unsensitizers include: mercaptotetrazoles such as 1-aryl or lower alkyl-5-mercaptotetrazoles, the lower alkyl moieties having 1 to 4 carbon atoms and the aryl moieties being of the naphthyl and phenyl series, and including 1-phenyl-5-mercaptotetrazole, 1-(α-naphthyl)-5-mercaptotetrazole, 1-ethyl-5-mercaptotetrazole and the like; a 2-mercaptobenzothiazole; a 2-mercaptobenzoxazole; or a mercaptotetrazaindene such as 7-mercapto-1,3,4,6-tetrazaindene and the like.

The amount of anti-unsensitizer utilized in the emulsions of the invention can be widely varied, although we more generally utilize about .01 to 5 mole percent, and preferably about .1 to 2 mole percent, based on the silver halide in the emulsion.

A wide variety of light-developable, direct-print photographic silver halide emulsions can be utilized in the present invention, such being well known to those skilled in the present art. Suitable silver halides include silver chloride, silver bromide, silver bromoiodide, silver chloroiodide, chlorobromide, and silver chlorobromoiodide. For a description of suitable emulsions, reference is made to Davey et al. U.S. Patent 2,592,250, issued Apr. 8, 1952; Glafkides, Photographic Chemistry, vol. 1, pp. 31–2, Fountain Press, London; and McBride Application, Ser. No. 222,964, filed Sept. 11, 1962, wherein is disclosed the preparation of silver halide emulsions with organic thioether silver halide solvents present during the grain growth of the silver halide. Generally about .1 to 25 g. of such thioethers per mole of silver halide is used. Typical of such thioethers are 3,6-dithia-1,8-octanediol, 1,10-dithia-4,7,13,16-tetraoxacyclooctadecane, 7,10-diaza-1,16-dicarboxamido-3,14-dithiahexadecane-6,11-dione, and 1,17-di-(N-ethylcarbamyl)-6,12-dithia-9-oxaheptadecane. The present silver halide emulsions generally have an average grain size of about .1 to 10 microns, and more generally about .5 to 1 micron.

The so-called "internal image" emulsions are particularly useful in the invention, such emulsions are prepared with silver halide grains wherein a substantial amount, and preferably a predominant amount, of the sensitivity to radiation is internal to the grains. Typically, such internal image emulsions are those which, when measured according to normal photographic techniques by coating a test portion of the emulsion on a transparent support, exposing to a light intensity scale having 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).

DEVELOPER A

	Grams
N-methyl-p-aminophenol sulfate	0.31
Sodium sulfite, desiccated	39.6
Hydroquinone	6.0
Sodium carbonate, desiccated	18.7
Potassium bromide	0.86
Citric acid	0.68
Potassium metabisulfite	1.5
Water to make 1 liter.	

DEVELOPER B

	Grams
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.	

A wide variety of hydrophilic, water-permeable organic colloids can be suitably utilized in preparing the silver halide emulsions or dispersions of the invention. Gelatin is preferably utilized although other colloidal material such as colloidal alubumin, cellulose derivatives, synthetic resins or the like can be utilized. Suitable colloids that can be used are polyvinyl alcohol or a hydrolyzed polyvinyl acetate as described in Lowe, U.S. Patent 2,286,215, issued June 16, 1942; a far hydrolyzed cellulose ester such as cellulose acetate hydrolyzed to an acetyl content of 19 to 26% as described in U.S. Patent 2,327,808 of Lowe and Clark, issued Aug. 24, 1943; a water-soluble ethanolamine cellulose acetate as described in Yutzy, U.S. Patent 2,322,085, issued June 15, 1943; a polyacrylamide having a combined acrylamide content of 30 to 60% and a specific viscosity of 0.25 to 1.5 on an imidized polyacrylamide of like acrylamide content and viscosity as described in Lowe, Minsk and Kenyon, U.S. Patent 2,541,474, issued Feb. 13, 1951; zein as described in Lowe, U.S. Patent 2,563,791, issued Aug. 7, 1951; a vinyl alcohol polymer containing urethane carboxylic acid groups of the type described in Unruh and Smith, U.S. Patent 2,768,154, issued Oct. 23, 1956; or containing cyano-acetyl groups such as the vinyl alcohol-vinyl cyanoacetate copolymer as described in Unruh, Smith and Priest, U.S. Patent 2,808,331, issued Oct. 1, 1957; or a polymeric material which results from polymerizing a protein or a saturated acylated protein with a monomer having a vinyl group as described in Illingsworth, Dann and Gates, U.S. Patent 2,852,382, issued Sept. 19, 1958.

The subject photodevelopable photographic silver halide emulsions of the invention can contain the addenda generally utilized in such products including gelatin hardeners, gelatin plasticizers, coating aids and the like.

The above-described emulsions of the invention can be coated on a wide variety of supports in accordance with usual practice. Typical supports for photographic elements of the invention include paper, cellulose nitrate film, cellulose acetate film, polyvinyl acetal film, polystyrene film, polyethyleneterephthalate film, polyethylene-coated paper, and related films of resinous materials and others.

Water-souble lead salts are preferably present during the grain growth of the silver halide of the present emulsions to form silver-lead halide grains which preferably contain about .01 to 5 mole percent lead based on the silver.

In forming a photodeveloped image with a typical photographic element having coated thereon an emulsion of the invention, the emulsion on the element is initially exposed to a high intensity light source to form a latent image in the emulsion, and thereafter the resulting latent image is photodeveloped by exposing it to a light source of less intensity than the original exposure. A typical instrument for exposing the emulsion of the invention is an oscillograph of the type described by Heiland in U.S. Patent 2,580,427, issued Jan. 1, 1952. Typical suitable high intensity light sources are mercury vapor lamps that have high blue and ultraviolet emission, xenon lamps that emit light of wavelengths similar to daylight, and tungsten lamps that have high red emission. The low intensity light source that is utilized to effect the photodevelopment after the high intensity exposure can be conventional fluorescent light, a tungsten light or even ordinary daylight.

When merocyanine dyes are utilized as the spectral sensitizing dyes in the emulsions of the invention, the dye is substantially bleached or made colorless during the photodevelopment step. Thus, the color or stain of the dye does not persist as objectionable background coloration in the nonimage or D_{min} areas after photodevelopment.

After exposure and photodevelopment, emulsions of the invention containing the above-described thiourea halogen acceptors can be chemically developed and fixed to make archival-quality records if desired. Emulsions containing halogen acceptors like stannous salts (e.g., stannous chloride) cannot be so readily developed and fixed as such halogen acceptors tend to cause fog during such a chemical processing.

The invention is further illustrated by the following examples of preferred examples thereof.

Example 1

A light-developable, direct-print, light-sensitive, gelatino-silver chlorobromide emulsion (95% bromide, 5% chloride) having silver halide grains of high internal sensitivity was prepared by slowly adding an aqueous solution of silver nitrate containing .85 g. of lead nitrate per mole of silver to an aqueous gelatin solution containing a stoichiometric excess of potassium chloride and potassium bromide to provide a large-grain emulsion, .5 g. of 1,8-dihydroxy-3,6-dithiaoctane per mole of silver being added during the silver halide precipitation. The emulsion was washed with water to remove water-soluble salts. The prepared emulsion was divided into several portions and to each portion of the emulsion was added a spectral sensitizing dye at a concentration of 120 mg. per mole of silver halide, potassium iodide at a concentration of 1.65 grams per mole of silver halide and 0.4 gram per mole of silver halide of the halogen acceptor, 1-n-butyl - 1,2,5,6-tetrahydro - 1,3,5-triazine-4-thiol. Additional similar emulsion portions were prepared except that the anti-unsensitizer, 1-phenyl-5-mercaptotetrazole, was also incorporated in the emulsions. The effect of the anti-unsensitizer on improving the effectiveness of the spectral sensitizing dye while keeping a high density differential between image and non-image areas after exposure to a high intensity light source and photodevelopment in the presence of a light source of less intensity was determined. More specifically, strips of each coating were exposed to a 100 microsecond flash on an Edgerton, Germeshausen and Grier Mark VI sensitometer through a 0.15 log E neutral density step tablet covered by a yellow filter (Wratten No. 16). Thereafter, the exposed strips were photodeveloped for five minutes to a 60 foot-candle cool-white fluorescent light source. In addition, another portion of each of the coatings was exposed to the equivalent of the sensitometer flash without any step tablet or filter and after photodevelopment through a 0.5 density increment step tablet to 2000 foot-candles of cool-white fluorescent light, the densities of the exposed and unexposed areas were measured through a Wratten No. 15 Filter and the differences recorded and summarized below in Table I as ΔD. Methanol or acetone were the dye solvents.

TABLE I

Dye	Visible 0.15 log E Steps on Exposure to Minus Blue Light and Photodevelopment		ΔD	
	Without Anti-unsens.	With Anti-unsens.	Without Anti-unsens.	With Anti-unsens.
A	0	10	.52	.55
B	2	10	.52	.54
C	2	10	.52	.50
D	6	15	.51	.54
E	0	11	.51	.53
F	6	17	.52	.50
G	0	15	.53	.52
H	2	14	.51	.53

In Table I above, the designated optical sensitizing dyes are set out below.

(A) 4-[(3-ethyl-2-benzoxazolinylidene)ethylidene]-3-methyl-2-thiohydantoin

(B) 3-ethyl-5-[(3-ethyl-2-benzoxazolinylidene)ethylidene]-1-phenyl-2-thiohydantoin

(C) 3-ethyl-5-[(3-ethyl-2-benzothiazolinylidene)isopropylidene]-2-thio-2,4-oxazolidinedione

(D) 5-[(3-ethyl-2-benzothiazolinylidene)ethylidene]-3-n-heptyl-1-phenyl-2-thiohydantoin

(E) 1-carboxymethyl-5-[(3-ethyl-2-benzoxalinylidene)ethylidene]-3-phenyl-2-thiohydantoin

(F) 5-[(1-ethylnaphtho{1,2-d}thiazolin-2-ylidene)ethylidene]-3-n-heptyl-1-phenyl-2-thiohydantoin

(G) 3,3',9-triethyl-5,5'-diphenyloxacarbocyanine iodide

(H) 9-ethyl-3,3'-di(β-methoxyethyl)-5,5'-diphenyloxacarbocyanine iodide

The number of visible 0.15 log E steps on exposure to white light and photodevelopment for the various samples ranged between 18 and 20. As can be observed from the data set out in Table I above, the anti-unsensitizer substantially improved the minus blue speed of the emulsions while maintaining a high ΔD. Suitable light-developable, direct-print, gelatino-silver halide emulsions to which the feature addenda are added can also be prepared as described in Davey et al., U.S. Patent 2,592,250, issued Apr. 8, 1952.

Example 2

Several light-developable, direct-print, light-sensitive gelatino-silver chlorobromide emulsions of the type described in Example 1 were prepared wherein each of the emulsions contained 120 mg. per mole of spectral sensitizing dye D described in Example 1, 1.6 grams of potassium iodide per mole of silver halide and 0.23 mole percent based on the silver halide of a thiourea halogen acceptor. Several similar coatings were prepared wherein the anti-unsensitizer, 1-phenyl-5-mercaptotetrazole, was also added

to illustrate the improved spectral sensitivity of the resulting emulsion. The various coatings were thereafter exposed to a high intensity flash, and thereafter photodeveloped as described in Example 1. The effect of the anti-unsensitizer on the improved sensitivity to minus blue light and the density differences between the background and image areas are summarized by the data set out in Table II below.

TABLE II

Halogen Acceptor	Visible 0.15 log E Steps on Exposure to Minus Blue Light and Photodevelopment		ΔD	
	Without Anti-unsens.	With Anti-unsens.	Without Anti-unsens.	With Anti-unsens.
I	13	16	.47	.56
II	3	14	.52	.55
III	13	15	.46	.55
IV	12	15	.43	.53
V	14	16	.41	.55
VI	15	16	.37	.52

The number of visible 0.15 log E steps on exposure to white light and photodevelopment for the various samples ranged between 18 and 20. In Table II above, the designated thiourea halogen acceptors are set out below.

(I) 2-imindazolinethione
(II) 1-n-butyl-1,2,5,6-tetrahydro-1,3,5-triazine-4-thiol
(III) 1-methyl-2-mercaptoimidazole
(IV) 1-methyl-2-imidazolinethione
(V) 1,3-dimethyl-2-imidazolinethione
(VI) 1,3-di(β-hydroxyethyl)-imidazoline-2-thione

Example 3

Several light-developable, direct-print, light-sensitive gelatino-silver chlorobromide emulsions of the type described in Example 1 were prepared containing an anti-unsensitizer at a concentration of 1.25 grams per mole of silver halide, 120 mg. per mole of silver halide of dye F identified in Example 1, 0.4 gram per mole of silver halide of 1-n-butyl-1,2,5,6-tetrahydro-1,3,5-triazine-4-thiol and 1.6 grams per mole of silver halide of potassium iodide. For purposes of comparison, several compounds closely related to the subject anti-unsensitizers were incorporated into sample coatings in lieu of the anti-unsensitizers. Also a coating containing no anti-unsensitizer was made and included in the test. Various coatings were thereafter exposed to a high-intensity light source and photodeveloped as described in Example 1. Table III below summarizes the results of the tests containing the various addenda described above.

TABLE III

Anti-Unsens.	Visible 0.15 log E Steps on Exposure and Photodevelopment		ΔD
	Minus Blue	White	
None	5	18	.52
VII	15	20	.33
VIII	9	18	.40
IX	6	18	.57
X	14	19	.53
XI	0	10	.42
XII	0	17	.11
XIII	4	18	.52
XIX	0	0	.02
XX	4	18	.52

In Table III above, the designated anti-unsensitizers are set out below.

(VII) 1-(α-naphthyl)-5-mercaptotetrazole
(VIII) 7-mercapto-1,3,4,6-tetrazaindene
(IX) 2-mercaptobenzoxazole
(X) 2-mercaptobenzothiazole

Other closely-related compounds substituted for the anti-unsensitizers of Table III are set out below.

(XI) 2-mercapto-4-methyl-5-nitrothiazole
(XII) 3-mercapto-1,2,4-triazole
(XIII) 2-mercapto-5-phenyl-1,3,4-oxadiazole
(XIX) 4 - amino - 6 - hydroxy-2-mercapto-5-nitroso-pyrimidine
(XX) 1-ethylnaphtho[1,2]-thiazoline-2-thione

Example 4

A series of light-developable, direct-print light-sensitive gelatino-silver chlorobromide emulsions of the type described in Example 1 containing a spectral sensitizing dye and various other addenda as described in Table IV below were coated at coverages of 258 mg. of silver per square foot and 560 mg. of gelatin per square foot and exposed on an Edgerton, Germeshausen and Grier Mark VII sensitometer containing a xenon flash lamp for 10 microseconds through a 0.15 log E density-increment neutral density step tablet and a yellow filter (Wratten No. 16) to filter out blue light. The coatings were then photodeveloped for 10 seconds to a 1700 foot-candle cool-white fluoroescent light. The number of 0.15 log E minus blue steps for the various coatings are summarized in Table IV. Also, the densities in D_{max} and D_{min} areas for the various coatings were obtained as described in Example 1 and set out in Table IV.

TABLE IV

Coating Addenda	Visible 0.15 log E Steps on Exposure to Minus Blue Light and Photodevelopment	$D_{max.}$	$D_{min.}$	ΔD
Dye+KI	8	.44	.13	.31
Dye+TU	5	.38	.14	.24
Dye+TU+KI	3	.63	.27	.36
Dye+TU+KI+PMT	7	.65	.25	.40

With respect to the coating addenda of Table IV above, "Dye" is 3 - carboxymethyl-5-[(3-methyl-2-thiazolinylidine)isopropylidene]rhodanine in the coatings at a concentration of 120 mg. per mole of silver halide, KI is potassium iodide in the coatings at a concentration of 1.66 g. per mole of silver halide. TU is thiourea in the coatings at a concentration of .23 mole percent based on the silver halide, and PMT is 1-phenyl-5-mercaptotetrazole in the coating at a concentration of 1.28 g. per mole of silver halide.

In Examples 1 to 4 above, the sensitometers used to effect the described high intensity exposure utilized xenon lamps. The various sample emulsions were coated on paper supports at coverages of 258 mg. of silver and 560 mg. of gelatin per square foot.

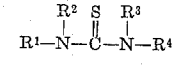
The present invention thus provides novel spectrally sensitized light-developable, direct-print, light-sensitive silver-halide emulsions.

The invention has been described in considerable detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

This application is a continuation-in-part application of U.S. Ser. No. 303,137 filed Aug. 19, 1963.

We claim:

1. A light-developable, direct-print silver halide emulsion spectrally sensitized with a sensitizing dye and containing at least about .01 mole percent of halogen acceptor per mole of silver halide having the formula



wherein:

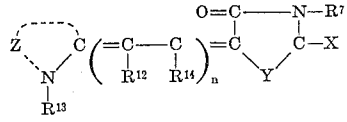
(A) R^1 and R^4 are each selected from the group consisting of
(1) a hydrogen atom,
(2) an acyl radical,

(3) a nitrogen-containing radical having a formula selected from the group consisting of $—NH_2$ and $—N=CH—R^5$ wherein R^5 is selected from the group consisting of an alkyl radical and an aryl radical,
(4) an alkyl radical, and
(5) an aryl radical;

(B) R^2 and R^3 are each selected from the group consisting of
(1) a hydrogen atom,
(2) an acyl radical,
(3) a nitrogen-containing radical having a formula selected from the group consisting of $—NH_2$ and $—N=CH—R^5$ wherein R^5 is selected from the group consisting of an alkyl radical and an aryl radical,
(4) an alkyl radical,
(5) an aryl radical, and
(6) together the necessary atoms to make a heterocyclic nucleus, said heterocyclic nucleus containing a carbon atom attached to at least one nitrogen atom of the thiourea grouping;

and at least about .1 mole percent of anti-unsensitizer per mole of silver halide selected from the group consisting of
(A) a mercaptotetrazole,
(B) a 2-mercaptobenzothioazole,
(C) a 2-mercaptobenzoxazole, and
(D) a mercaptotetrazaindene.

2. A light-developable, direct-print silver halide emulsion containing a merocyanine spectral sensitizing dye having the formula



wherein:
(A) R^7, R^{12} and R^{14} are each selected from the group consisting of
(1) an alkyl radical,
(2) an aryl radical, and
(3) a hydrogen atom;
(B) X is selected from the group consisting of
(1) a sulfur atom, and
(2) a selenium atom;
(C) Y is selected from the group consisting of
(1) an oxygen atom,
(2) a sulfur atom,
(3) a selenium atom,
(4) a group having the formula

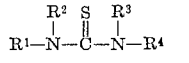


wherein R^{10} can be the substituents of R^7, and
(5) a group having the formula



wherein R^{11} can be the substituents of R^7;
(D) *n* is an integer of 0 to 2;
(E) R^{13} is selected from the group consisting of
(1) an alkyl radical, and
(2) an aryl radical; and
(F) Z represents the atoms required to form a basic heterocyclic nucleus;

at least about .01 mole percent having the formula halogen acceptor per mole of silver halide of



wherein:
(A) R^1 and R^4 are each selected from the group consisting of
(1) a hydrogen atom,

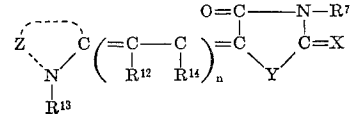
(2) an acyl radical,
(3) a nitrogen-containing radical having a formula selected from the group consisting of $—NH_2$ and $—N=CH—R^5$ wherein R^5 is selected from the group consisting of an alkyl radical and an acyl radical,
(4) an alkyl radical, and
(5) an aryl radical;

(B) R^2 and R^3 are each selected from the group consisting of
(1) a hydrogen atom,
(2) an acyl radical,
(3) a nitrogen-containing radical having a formula selected from the group consisting of $—NH_2$ and $—N=CH—R^5$ wherein R^5 is selected from the group consisting of an alkyl radical and an acyl radical,
(4) an alkyl radical,
(5) an aryl radical, and
(6) together the necessary atoms to make a heterocyclic nucleus, said heterocyclic nucleus containing a carbon atom attached to at least one nitrogen atom of the thiourea grouping;

and at least about .1 mole percent of anti-unsensitizer per mole of silver halide selected from the group consisting of
(A) a mercaptotetrazole,
(B) a 2-mercaptobenzothiazole,
(C) a 2-mercaptobenzoxazole, and
(D) a mercaptotetrazaindene.

3. A light-developable, direct-print silver halide emulsion as described in claim **2** that contains a water-soluble iodide.

4. A light-developable, direct-print silver halide emulsion containing a merocyanine spectral sensitizing dye having the formula



wherein:
(A) R^7, R^{12} and R^{14} are each selected from the group consisting of
(1) an alkyl radical,
(2) an aryl radical, and
(3) a hydrogen atom;
(B) X is selected from the group consisting of
(1) a sulfur atom, and
(2) a selenium atom;
(C) Y is selected from the group consisting of
(1) an oxygen atom,
(2) a sulfur atom,
(3) a selenium atom,
(4) a group having the formula

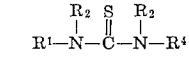


wherein R^{10} can be the substituents of R^7, and
(5) a group having the formula



wherein R^{11} can be the substituents of R^7;
(D) *n* is an integer of 0 to 2;
(E) R^{13} is selected from the group consisting of
(1) an alkyl radical, and
(2) an aryl radical; and
(F) Z represents the atoms required to form a basic heterocyclic nucleus;

and at least about .01 mole percent of a halogen acceptor per mole of silver halide having the formula



wherein:

(A) R^1 and R^4 are each selected from the group consiting of

(1) a hydrogen atom,

(2) an acyl radical,

(3) a nitrogen-containing radical having a formula selected from the group consisting of $—NH_2$ and —N=CH—R^5 wherein R^5 is selected from the group consisting of an alkyl radical and an acyl radical,

(4) an alkyl radical, and

(5) an aryl radical;

(B) R^2 and R^3 are each selected from the group consisting of

(1) a hydrogen atom,

(2) an acyl radical,

(3) a nitrogen-containing radical having a formula selected from the group consisting of $—NH_2$ and —N=CH—R^5 wherein R^5 is selected from the group consisting of an alkyl radical and an acyl radical,

(4) an alkyl radical,

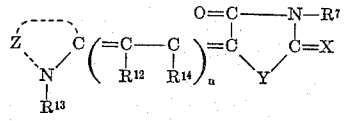
(5) an aryl radical, and

(6) together the necessary atoms to make a heterocyclic nucleus, said heterocyclic nucleus containing a carbon atom attached to at least one nitrogen atom of the thiourea grouping;

and at least about .1 mole percent of a mercaptotetrazole anti-unsensitizer per mole of silver halide.

5. A light-developable, direct-print silver halide emulsion as described in claim 4 wherein the mercaptotetrazole anti-unsensitizer is 1-phenyl-5-mercaptotetrazole.

6. A light-developable, direct-print silver halide emulsion containing at least about .01 mole percent of a triazine-4-thiol halogen acceptor per mole of silver halide; a merocyanine spectral sensitizing dye having the formula



wherein:

(A) R^7, R^{12} and R^{14} are each selected from the group consisting of

(1) an alkyl radical,

(2) an aryl radical, and

(3) a hydrogen atom;

(B) X is selected from the group consisting of

(1) a sulfur atom, and

(2) a selenium atom;

(C) Y is selected from the group consisting of

(1) an oxygen atom,

(2) a sulfur atom,

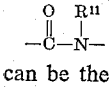
(3) a selenium atom,

(4) a group having the formula



wherein R^{10} can be the substituents of R^7, and

(5) a group having the formula



wherein R^{11} can be the substituents of R^7;

(D) *n* is an integer of 0 to 2;

(E) R^{13} is selected from the group consisting of

(1) an alkyl radical, and

(2) an aryl radical; and

(F) Z represents the atoms required to form a basic heterocyclic nucleus;

and an at least about .1 mole percent of anti-unsensitizer per mole of silver halide selected from the group consisting of

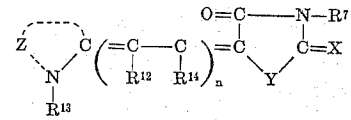
(A) a mercaptotetrazole,

(B) a 2-mercaptobenzothiazole,

(C) a 2-mercaptotetrazole, and

(D) a mercaptotetrazaindene.

7. A light-developable, direct-print silver halide emulsion containing at least about .01 mole percent of thiourea per mole of silver halide; a merocyanine spectral sensitizing dye having the formula



wherein:

(A) R^7, R^{12} and R^{14} are each selected from the group consisting of

(1) an alkyl radical,

(2) an aryl radical, and

(3) a hydrogen atom;

(B) X is selected from the group consisting of

(1) a sulfur atom, and

(2) a selenium atom;

(C) Y is selected from the group consisting of

(1) an oxygen atom,

(2) a sulfur atom,

(3) a selenium atom,

(4) a group having the formula



wherein R^{10} can be the substituents of R^7, and

(5) a group having the formula



wherein R^{11} can be the substituents of R^7;

(D) *n* is an integer of 0 to 2;

(E) R^{13} is selected from the group consisting of

(1) an alkyl radical, and

(2) an aryl radical; and

(F) Z represents the atoms required to form a basic heterocyclic nucleus;

and an at least about .1 mole percent of anti-unsensitizer per mole of silver halide selected from the group consisting of

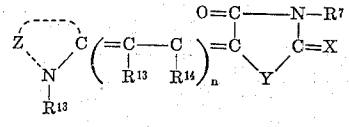
(A) a mercaptotetrazole,

(B) a 2-mercaptobenzothiazole,

(C) a 2-mercaptobenzoxazole, and

(D) a mercaptotetrazaindene.

8. A light-developable, direct-print silver halide emulsion containing at least about .01 mole percent of a 2-imidazolethione halogen acceptor per mole of silver halide; a merocyanine spectral sensitizing dye having the formula



wherein:

(A) R^7, R^{12} and R^{14} are each selected from the group consisting of

(1) an alkyl radical,

(2) an aryl radical, and

(3) a hydrogen atom;

(B) X is selected from the group consisting of

(1) a sulfur atom, and

(2) a selenium atom;

(C) Y is selected from the group consisting of

(1) an oxygen atom,

(2) a sulfur atom,

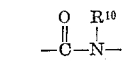
(3) a selenium atom,

(4) a group having the formula



wherein R^{10} can be the substituents of R^7, and

(5) a group having the formula



wherein R^{11} can be the substituents of R^7;

(D) n is an integer of 0 to 2;

(E) R^{13} is selected from the group consisting of

(1) an alkyl radical, and

(2) an aryl radical; and

(F) Z represents the atoms required to form a basic heterocyclic nucleus;

and an at least about .1 mole percent of anti-unsensitizer per mole of silver halide selected from the group consisting of

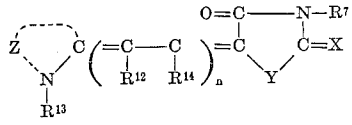
(A) a mercaptotetrazole,

(B) a 2-mercaptobenzothiazole,

(C) a 2-mercaptobenzoxazole, and

(D) a mercaptotetrazaindene.

9. A light-developable, direct-print silver halide emulsion containing at least about .01 mole percent of a 2-imidazolinethione halogen acceptor per mole of silver halide; a merocyanine spectral sensitizing dye having the formula



wherein:

(A) R^7, R^{12} and R^{14} are each selected from the group consisting of

(1) an alkyl radical,

(2) an aryl radical, and

(3) a hydrogen atom;

(B) X is selected from the group consisting of

(1) a sulfur atom, and

(2) a selenium atom;

(C) Y is selected from the group consisting of

(1) an oxygen atom,

(2) a sulfur atom,

(3) a selenium atom,

(4) a group having the formula



wherein R^{10} can be the substituents of R^7, and

(5) a group having the formula



wherein R^{11} can be the substituents of R^7;

(D) n is an integer of 0 to 2;

(E) R^{13} is selected from the group consisting of

(1) an alkyl radical, and

(2) an aryl radical; and

(F) Z represents the atoms required to form a basic heterocyclic nucleus;

and an at least about .1 mole percent of anti-unsensitizer per mole of silver halide selected from the group consisting of

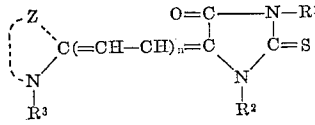
(A) a mercaptotetrazole,

(B) a 2-mercaptobenzothiazole,

(C) a 2-mercaptobenzoxazole, and

(D) a mercaptotetrazaindene.

10. A light-developable, direct-print silver halide emulsion containing a merocyanine spectral sensitizing dye having the formula



wherein:

(A) R^1 is an alkyl radical;

(B) R^2 is a phenyl radical;

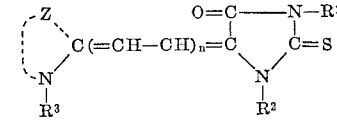
(C) n is an integer of 0 to 2;

(D) R^3 is an alkyl radical;

(E) Z represents the necessary atoms to form a benzothiazole nucleus;

at least about .01 mole percent of a triazine-4-thiol halogen acceptor per mole of silver halide; and at least about .1 mole percent of a mercaptotetrazole anti-unsensitizer per mole of silver halide.

11. A light-developable, direct-print silver halide emulsion containing a merocyanine spectral sensitizing dye having the formula



wherein:

(A) R^1 is an alkyl radical;

(B) R^2 is a phenyl radical;

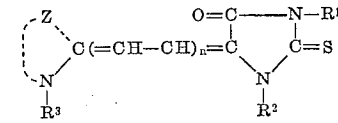
(C) n is an integer of 0 to 2;

(D) R^3 is an alkyl radical;

(E) Z represents the necessary atoms to form a naphthothiazole nucleus;

at least about 0.1 mole percent of a triazine-4-thiol halogen acceptor per mole of silver halide; and at least about .1 mole percent of a mercaptotetrazole anti-unsensitizer per mole of silver halide.

12. A light-developable, direct-print silver halide emulsion containing a merocyanine spectral sensitizing dye having the formula



wherein:

(A) R^1 is an alkyl radical;

(B) n is an integer of 0 to 2;

(C) R^2 is an alkyl radical;

(D) Z represents the necessary atoms to form a benzoxazole nucleus;

at least about .01 mole percent of a triazine-4-thiol halogen acceptor per mole of silver halide; and at least about .1 mole percent of a mercaptotetrazole anti-unsensitizer per mole of silver halide.

13. A light-developable, direct-print gelatino-silver halide emulsion comprising silver halide grains having a substantial amount of sensitivity internal to said grains, about .01 to 25 mole percent based on said silver halide of 1-methyl-2-mercapto-imidazole, about 10 to 1000 mg. per mole of said silver halide of 5-[(3-ethyl-2-benzothiazolinylidene) - ethylidene]-3-n-heptyl-1-phenyl-2-thiohydantoin, about .01 to 5 mole percent based on said silver halide of 1-phenyl-5-mercaptotetrazole, and about .05 to 10 mole percent based on said silver halide of potassium iodide.

14. A light-developable, direct-print gelatino-silver halide emulsion comprising silver halide grains having a substantial amount of sensitivity internal to said grains, about .01 to 25 mole percent based on said silver halide of 2-imidazolinethione, about 10 to 1000 mg. per mole of said silver halide of 5-[(3-ethyl-2-benzothiazolinylidene)ethylidene]-3-n-heptyl-1-phenyl-2-hydantoin, about 0.1 to 5 mole percent based on said silver halide of 1-phenyl-5-mercaptotetrazole, and about .05 to 10 mole percent based on said silver halide of potassium iodide.

15. A light-developable, direct-print gelatino-silver halide emulsion comprising silver halide grains having a substantial amount of sensitivity internal to said grains, about .01 to 25 mole percent based on said silver halide

of 1-n-butyl-1,2,5,6-tetrahydro-1,3,5-triazine-4-thiol, about 10 to 1000 mg. per mole of said silver halide of 5-[(1-ethylnaphtho{1,2 - d}thiazolin-2-ylidene)ethylidene]-3-n-heptyl-1-phenyl-2-thiohydantoin, about .01 to 5 mole percent based on said silver halide of 1-phenyl-5-mercaptotetrazole, and about .05 to 10 mole percent based on said silver halide of potassium iodide.

16. A light-developable, direct-print gelatino-silver halide emulsion comprising silver halide grains having a substantial amount of sensitivity internal to said grains, about .01 to 25 mole percent based on said silver halide of 1-n-butyl-1,2,5,6-tetrahydro-1,3,5-triazine-4-thiol, about 10 to 1000 mg. per mole of said silver halide of 5-[(1-ethylnaptho{1,2 - d}thiazolin-2-ylidene)ethylidene]-3-n-heptyl-1-phenyl-2-thiohydantoin, about .01 to 5 mole percent based on said silver halide of 1-(α-naphthyl)-5-mercaptotetrazole, and about .05 to 10 mole percent based on said silver halide of potassium iodide.

17. A light-developable, direct-print gelatino-silver halide emulsion comprising silver halide grains having a substantial amount of sensitivity internal to said grains, about .01 to 25 mole percent based on said silver halide of 1-n-butyl-1,2,5,6-tetrahydro-1,3,5-triazine-4-thiol, about 10 to 1000 mg. per mole of said silver halide of 5-[(1-ethylnaphtho{1,2 - d}thiazolin-2-ylidene)ethylidene]-3-n-heptyl-1-phenyl-2-thiohydantoin, about .01 to 5 mole percent based on said silver halide of 2-mercaptobenzothiazole, and about .05 to 10 mole percent based on said silver halide of potassium iodide.

18. A light-developable, direct-print gelatino-silver halide emulsion comprising silver halide grains having a substantial amount of sensitivity internal to said grains, about .01 to 25 mole percent based on said silver halide of 1-n-butyl-1,2,5,6-tetrahydro-1,3,5-triazine-4-thiol, about 10 to 1000 mg. per mole of said silver halide of 5-[(1-ethylnaphtho{1,2 - d}thiazolin-2-ylidene)ethylidene]-3-n-heptyl-1-phenyl-2-thiohydantoin, about .01 to 5 mole percent based on said silver halide of 2-mercaptobenzoxazole,

and about .05 to 10 mole percent based on said silver halide of potassium iodide.

19. A light-developable, direct-print gelatino-silver halide emulsion comprising silver halide grains having a substantial amount of sensitivity internal to said grains, about .01 to 25 mole percent based on said silver halide of 1-n-butyl-1,2,5,6-tetrahydro-1,3,5-triazine-4-thiol, about 10 to 1000 mg. per mole of said silver halide of 5-[(1-ethylnaphtho{1,2-d}thiazolin - 2 - ylidene)ethylidene]-3-n-heptyl-1-phenyl-2-thiohydantoin, about .01 to 5 mole percent based on said silver halide of 7-mercapto-1,3,4,6-tetrazaindene, and about .05 to 10 mole percent based on said silver halide of potassium iodide.

20. A light-developable, direct-print gelatino-silver halide emulsion comprising silver halide grains having a substantial amount of sensitivity internal to said grains, about .01 to 25 mole percent based on said silver halide of thiourea, about 10 to 1000 mg. per mole of said silver halide of 3 - carboxymethyl-5-[(3-methyl-2-thiazolinylidine)isopropylidene]rhodanine, about .01 to 5 mole percent based on said silver halide of 1-phenyl-5-mercaptotetrazole, and about .05 to 10 mole percent based on said silver halide of potassium iodide.

21. A light-developable, direct-print silver halide emulsion as described in claim **2** prepared with an organic thioether silver halide solvent present during the grain growth of the silver halide.

References Cited

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J. H. RAUBITSCHEK, *Assistant Examiner.*

UNITED STATES PATENT OFFICE

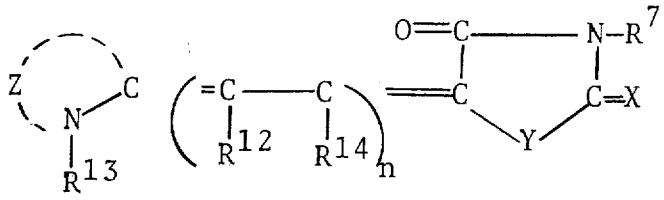
CERTIFICATE OF CORRECTION

Patent No. 3,367,780 February 6, 1968

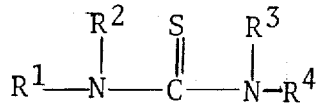
Delbert D. Fix et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

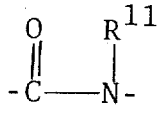
Column 11, lines 33 to 38, the formula should appear as shown below instead of as in the patent:



column 12, lines 72 to 75, the formula should appear as shown below instead of as in the patent:



column 15, lines 2 and 3, the formula should appear as shown below instead of as in the patent:



column 16, line 69, for "0.1" read -- .01 --.

Signed and sealed this 22nd day of July 1969.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents