United States Patent Office

3,287,136

Patented Nov. 22, 1966

3,287,136

LIGHT-DEVELOPABLE SILVER HALIDE EMULSIONS

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No Drawing. Filed Sept. 2, 1964, Ser. No. 394,062
15 Claims. (Cl. 96—106)

This application is a continuation-in-part of my copending application, Serial No. 222,964, filed on September 11, 1962, and now abandoned.

The present invention relates to photography, and more particularly to spectrally sensitized 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 chemical 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.

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 photographic elements having high sensitivity to light of wavelengths longer than blue light.

It is also an object of this invention to provide novel photographic light-developable, direct-print silver halide emulsions that can be exposed to a high-intensity trace and thereafter photodeveloped to produce images particularly characterized as having low D_{min} or background density.

It is likewise an object of this invention to provide photographic light-developable, direct-print silver halide emulsions containing novel cooperating or synergistic addenda for such emulsions.

These and other objects of the invention are accomplished with light-developable, direct-print silver halide emulsions sensitized with a spectral sensitizing dye and wherein the silver halide grains of the emulsion are formed in the presence of lead ions. The spectral sensitizing dye and the lead moiety in such emulsions cooperate or synergize to produce particularly useful light-developable, direct-print emulsions.

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, and silver chlorobromoiodide. The preferred emulsions are those that are predominantly bromide. For a description of suitable emulsions, reference is made to Davey et al., U.S. Patent 2,592,250, issued April 8, 1952; Glafkides, Photographic Chemistry, vol. 1. pp. 31–2, Fountain Press, London; and my application, Serial No. 222,964, filed September 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. In application Serial No. 222,964 is taught the addition of the thioether silver halide solvent to the colloidal material in which the silver halide is precipitated, during the precipitation of the silver halide, or to the silver halide prior to or during the ripening of the silver halide. Typical of such thioethers include 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 amount of thioether utilized to prepare the silver halide emulsions described in my application, Serial No. 222,964, can be widely varied although about .1 to 25 g. of thioether per mole of silver halide is generally utilized. 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 used in the invention, such having silver halide grains wherein a predominant amount of the sensitivity to radiation is internal to the grains. 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

	G.
N-methyl-p-aminophenol sulfate	0.31
Sodium sulfite, desiccated	39.60
Hydroquinone	6.00
Sodium carbonate, desiccated	18.70
Potassium bromide	0.86
Citric acid	0.68
Potassium metabisulfite	1.60

Water to make 1 liter.

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

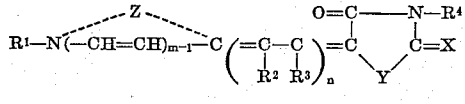
Water to make 1 liter.

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 albumin, 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 19–26% as described in U.S. Patent 2,327,808 of Lowe and Clark, issued August 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 February 13, 1951; as described in Lowe, U.S. Patent 2,563,791, issued August 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 October 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 October 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 September 19, 1958.

Lead ions are used in the precipitation or formation of the silver halide of the emulsions of the invention. Water-soluble lead salts are suitably added with the water-soluble silver salt to an appropriate water-soluble halide to precipitate the lead-silver halide of the present emulsions. Typical suitable water-soluble lead or plumbous salts include lead acetate, lead nitrate, lead cyanide, and the like water-soluble lead salts. The amount of lead utilized in the silver halide of the emulsions of the invention suitably ranges from about .01 to 5 mole percent based on the silver. The presence of a water-soluble lead salt during the silver halide formation or grain growth when preparing the light-developable, direct-print emulsions of the invention is to be distinguished from the addition of a water-soluble lead salt shortly prior to coating and after the silver halide grains have been formed.

Sensitizing amounts of merocyanine or cyanine dyes are utilized to spectrally sensitize the present emulsions.

Particularly useful merocyanine dyes have the formula



wherein X can be a sulfur or a selenium atom; R^1, R^2, R^3 and R^4 are each an alkyl radical (e.g., methyl, ethyl, carbethoxymethyl, carboxymethyl, benzyl (phenylmethyl), β-sulfoethyl, butyl, etc.), an aryl radical, such as phenyl, tolyl, etc., and R^2, R^3 and R^4 can also be a hydrogen atom; Y is an oxygen atom, a sulfur atom, a selenium atom,



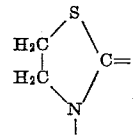
wherein R^5 can be any of the substituents of R^4, and

wherein R^6 can be any of the substituents of R^4; m is a positive integer of 1 or 2 and preferably 1; n is a positive integer of 0, 1 or 2; and Z represents the nonmetallic atoms required to complete a basic hetercyclic nucleus generally having 5 to 6 atoms in the heterocyclic ring such as carbon, sulfur, selenium, oxygen and nitrogen to form such moieties as those selected from the group consisting of those of the thiazole series (e.g., thiazole, 4-methylthiazole, 5-methylthiazole, 4-phenylthiazole, 5-phenylthiazole, 4,5-dimethylthiazole, 4,5-diphenylthiazole, 4-(2-thienyl)thiazole, etc.), those of the benzothiazole series (e.g., benzothiazole, 4-chlorobenzothiazole, 5-chlorobenzothiazole, 6-chlorobenzothiazole, 7-chlorobenzothiazole, 4-methylbenzothiazole, 5-methylbenzothiazole, 6-methylbenzothiazole, 5-bromobenzothiazole, 6-bromobenzothiazole, 4-phenylbenzothiazole, 5-phenylbenzothiazole, 4-methoxybenzothiazole, 5-methoxybenzothiazole, 6-methoxybenzothiazole, 5-iodobenzothiazole, 6-iodobenzothiazole, 4-ethoxybenzothiazole, 5-ethoxybenzothiazole, tetrahydrobenzothiazole, 5,6-dimethoxybenzothiazole, 5,6-dioxymethylenebenzothiazole, 5-hydroxybenzothiazole, 6-hydroxybenzothiazole, etc.), those of the naphthothiazole series (e.g., α-naphthothiazole, β-naphthothiazole, 5-methoxy-β-napthothiazole, 5-ethoxy-β-napthothiazole, 7-methoxy-α-naphthothiazole, 8-methoxy-α- naphthothiazole, etc.), those of the thianaphtheno-7′,6′,4,5-thiazole series (e.g., 4′-methoxythianaphtheno-7′,6′,4,5-thiazole, etc.), those of the oxazole series (e.g., 4-methyloxazole, 5-methyloxazole, 4-phenyloxazole, 4,5-diphenyloxazole, 4-ethyloxazole, 4,5-dimethyloxazole, 5-phenyloxazole, etc.), those of the benzoxazole series (e.g., benzoxazole, 5-chlorobenzoxazole, 5-phenylbenzoxazole, 5-methylbenzoxazole, 6-methylbenzoxazole, 5,6-dimethylbenzoxazole, 4,6-dimethylbenzoxazole, 5-methoxybenzoxazole, 6-methoxybenzoxazole, 5-ethoxybenzoxazole, 6 - chlorobenzoxazole, 5 - hydroxybenzoxazole, 6-hydroxybenzoxazole, etc.), those of the naphthoxazole series (e.g., α-naphthoxazole, β-naphthoxazole, etc.), those of the selenazole series (e.g., 4-methylselenazole, 4-phenylselenazole, etc.), those of the benzoselenazole series (e.g., benzoselenazole, 5-chlorobenzoselenazole, 5-methoxybenzoselenazole,, 5-hydroxybenzoselenazole, tetrahydrobenzoselenazole, etc.), those of the naththoselenazole series (e.g., α-naphthoselenazole, β-naphthoselenazole, etc.), those of the thiazoline series (e.g., thiazoline, 4-methylthiazoline, etc.), those of the 2-quinoline series (e.g., quinoline, 3-methylquinoline, 5-methylquinoline, 7-methylquinoline, 8-methylquinoline, 6-chloroquinoline, 8-chloroquinoline, 6-methoxyquinoline, 6-ethoxyquinoline, 6-hydroxyquinoline, 8-hydroxyquinoline, etc.), those of the 4-quinoline series (e.g., quinoline, 6-methoxyquinoline,, 7-methylquinoline, 8-methylquinoline etc.), those of the 1-isoquinoline series (e.g., isoquinoline, 3,4-dihydroisoquinoline, etc.), those of the 3,3-dialkylindolenine series (e.g., 3,3-dimethylindolenine, 3,3,5-trimethylindolenine, 3,3,7-trimethylindolenine, etc.), those of the 2-pyridine series (e.g., pyridine, 3-methylpyridine, 4-methylpyridine, 5-methylpyridine, 6-methylpyridine, 3,4-dimethyl pyridine, 3,5-dimethylpyridine, 3,6-dimethylpyridine, 4,5-dimethylpyridine, 4,6-dimethylpyridine, 4-chloropyridine, 5-chloropyridine, 6-chloropyridine, 3-hydroxypyridine, 4-hydroxypyridine, 5-hydroxypyridine, 6-hydroxypyridine, 3-phenylpyridine, 4-phenylpyridine, 6-phenylpyridine, etc.), those of the 4-pyridine series (e.g., 2-methylpyridine, 3-methylpyridine, 2-chloropyridine, 3-chloropyridine, 2,3-dimethylpyridine, 2,5-dimethylpyridine, 2,6-dimethylpyridine, 2-hydroxypyridine, 3-hydroxypyridine, etc.), those of the 1-substituted imidazole series (e.g., 1-ethylimidazole, 1-ethyl-4-phenylimidazole, 1,4-dimethylimidazole, 4-methyl-1-phenylimidazole, etc.), those of the 1-substituted

benzimidazole series (e.g., 1-ethylbenzimidazole, 1-butylbenzimidazole, 1-ethyl-4,5-dichlorobenzimidazole, etc.), those of the 1-substituted naphthimidazole series (e.g., 1-methyl-α-naphthimidazole, 1-ethyl-α-naphthimidazole, 1-butyl-β-naphthimidazole, 6-chloro-1-methyl-α-naphthimidazole, etc.), etc. The Y substituent is preferably



to form a thiohydantoin nucleus. When Y is a sulfur atom, the heterocyclic moiety completed by the substituent Z is other than a thiazoline group,

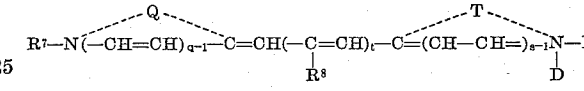


when *n* is 1. At least one of the substituents R^4, R^5 or R^6 is preferably a higher alkyl radical or a hydrogen atom. The alkyl substituents in the described dyes can be widely varied although alkyls having 1 to 18 carbon atoms are more generally used, those alkyls denominated "lower" alkyls having 1 to 4 carbon atoms and those alkyls denominated "higher" alkyls having 5 to 18 and preferably 7 to 18 carbon atoms. The alkyl and aryl radicals of the described dyes can be substituted or unsubstituted. Also useful in my invention are the holopolar dyes represented by Formula I in U.S. Patent 2,739,964 (reissued as 24,292).

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

5 - [(3 - ethyl - 2 - benzothiazolinylidene)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)-3-heptyl-1-phenyl-2-thiohydantoin
3 - ethyl - 5 - [(3-ethyl-2-benzoxazolinylidene)isopropylidene]-2-thio-2,4-oxazolidinedione
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 - [(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
3 - heptyl-5-(1-methylnaphtho{1,2-d}thiazolin-2-ylidene)-1-phenyl-2-thiohydantoin

Typical suitable cyanine dyes have the formula



wherein Q and T are the same substituents as the Z substituent for the above-described merocyanine dyes, *q* and *s* are positive integers of 1 or 2 and preferably 1, *t* is a positive integer of 0 to 2, D is an acid anion such as chloride, bromide, iodide, perchlorate, thiocyanate, acetate, methylsulfate, ethylsulfate, benzenesulfonate, toluenesulfonate or the like, R^8 is the same substituent as the R^2 and R^3 substituents for the above-described merocyanine dyes, and R^7 and R^9 are the same substituents as the R^1 substituent for the above-described merocyanine dyes.

Typical useful cyanine dyes that can be used to spectrally 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'-diethyl-9-methyl-5,5'-diphenyloxacarbocyanine bromide 3-methyl-1'-ethylthia-2'-cyanine iodide
3,3',9-triethyl-5,5'-diphenyloxacarbocyanine iodide
9 - ethyl - 3,3'-di(β-methoxyethyl)-5,5-diphenyloxacarbocyanine iodide
anhydro - 3 - ethyl-5-phenyl-1'-(4-sulfobutyl)thia-4'-carbocyanine hydroxide
1'-butyl-3-ethylselena-4'-carbocyanine iodide
1'-butyl-3-ethyl-4-phenylthia-4'-carbocyanine iodide
1',3-diethyloxa-4'-cyanine iodide
1',3-diethyl-4,5-benzothia-2'-cyanine iodide
1-ethyl-1'-isopropyl-2,4'-cyanine perchlorate
1',3-diethylthia-4'-pyridocyanine iodide
1-ethyl-1',8'-ethylene-2,4'-cyanine iodide
1-ethyl-1,3,3-trimethylindo-4'-cyanine iodide

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

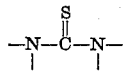
The sensitizing amount of the spectral sensitizing dyes utilized can be widely varied. The concentration of the

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 dye or combinations of several dyes can be used in the present emulsions for spectral sensitization.

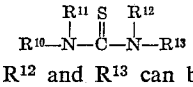
Merocyanine spectral sensitizing dyes are preferably utilized in the emulsions of the invention as stain imparted to emulsions containing such dyes is substantially bleached or made colorless during photodevelopment. Also, mercocyanine dyes tend to be less easily displaced or desorbed from the silver halide crystals of the emulsions of the invention than cyanine dyes by many halogen acceptors that are utilized in light-developable, direct-print silver halide emulsions.

A wide variety of halogen acceptors can be utilized in the emulsions of the invention.

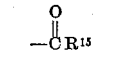
A particularly useful class of halogen acceptors are thiourea compounds including thiourea itself and fully or partially substituted thioureas which include the thiourea grouping



Typical suitable thioureas have the structure



wherein R^{10}, R^{11}, R^{12} and R^{13} can be hydrogen atoms, alkyl radicals, aryl radicals such as those of the phenyl and naphthyl series, nitrogen-containing radicals such as amino radicals ($—NH_2$) and $—N=CH—R^{14}$ wherein R^{14} is an alkyl or an aryl radical such as those of the naphthyl and phenyl series, acyl radicals



wherein R^{15} is an alkyl or an aryl radical such as those of the naphthyl and phenyl series; and R^{11} and R^{12} can together be the necessary atoms to complete a heterocyclic nucleus with the thiourea grouping to form such cyclic compounds as an imidazole-thione, an imidazoline-thione, a triazine-thiol, 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.

Typical suitable thiourea compounds that can be utilized as halogen acceptors in the emulsions of the invention include:

1-methyl-2-imidazolethione
1-n-butyl-1,2,5,6-tetrahydro-1,3,5-triazine-4-thiol
Thiourea
1-methyl-2-imidazolinethione
D-mannose thiosemicarbazone
Morpholino-2-propane thiosemicarbazone
D-galactose thiosemicarbazone
1,3-dimethyl-2-imidazolinethione
2-imidazolinethione
1-phenyl-5-mercaptotetrazole
Thiosemicarbazide
Tetramethylthiourea
p-Dimethylaminobenzaldehyde-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-4-imidazoline-2-thione
1-(o-methoxyphenyl)-2-thiourea

Other suitable halogen acceptors include stannous salts such as stannous chloride as disclosed in Hunt, U.S. Patent 3,033,678, issued May 8, 1962; aromatic mercaptans such as thiosalicylic acid; hydroquinones such as hydroquinone, chlorohydroquinone, gentisic acid and t-butylhydroquinone; catechols such as phenyl catechol and t-butylcatechol; p-aminophenols such as N-methyl-p-aminophenol sulfate; 3-pyrazolidones such as 1-phenyl-3-pyrazolidone, 4-methyl-1-phenyl-3-pyrazolidone and 1-phenyl-4,4-dimethyl-3-pyrazolidone; and the like halogen acceptors well known to those skilled in the art.

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.

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, based on the silver halide in the emulsion is utilized. Water-soluble iodides are particularly useful. Illustrative water-soluble halides include ammonium, calcium, lithium, magnesium, potassium, or sodium bromide, chloride or iodide.

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, polyethyene-coated paper, and related films of resinous materials and others.

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, short-duration 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 January 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 light 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.

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

Example 1

A light-developable, direct-print, light-sensitive, large grain gelatine-silver chlorobromide emulsion (95 mole

percent bromide, 5 mole percent 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 agitated aqueous gelatin solution containing a stoichiometric excess of potassium chloride and potassium bromide, .5 g. of the silver halide solvent, 1,8-dihydroxy-3,6-dithiaoctane, per mole of silver also being added during the silver halide precipitation. The emulsion was washed with water to remove water-soluble salts. The prepared emulsion was divided up into several portions and to each portion of the emulsion was added a spectral sensitizing dye in acetone or methanol at a concentration of 120 mg. per mole of silver halide, 400 mg. of 1-n-butyl-1,2,5,6-tetrahydro-1,3,5-triazine-4-thiol in methanol per mole of silver halide and 1.6 grams of potassium iodine per mole of silver halide. The resulting emulsions were coated on paper supports at a silver coverage of 260 mg. per square foot and at a gelatin coverage of 560 mg. per square foot. Strips of each coating containing various spectral sensitizing dyes were 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 followed by a photodevelopment of 5 minutes with a 60 foot-candle cool white fluorescent light. Table I below summarizes the number of 0.15 log E neutral density steps for the various dyes utilized in the test, this giving indication of over-all white light speed. Other portions of the various test coatings were also exposed through the described step tablets containing a yellow filter (Wratten No. 16) to filter out blue light. This latter test indicated the speed to minus blue light and the effect of the optical sensitizing dye. The number of 0.15 log E minus blue steps is also summarized by the data set out in Table I below.

TABLE I

Dye	Visible 0.15 log E Steps On Exposure and Photodevelopment	
	Minus Blue	White
None	0	18
a	9	19
b	9	19
c	6	19
d	6	19
e	11	20

In Table I above, and hereafter, the optical sensitizing dyes referred to as dyes *a–e* are as set out below:

(*a*) 5-[(3ethyl-2-benzothiazolinylidene)ethylidene] rhodanine

(*b*) 5-[(3-ethyl-2-benzothiazolinylidene)ethylidene]-2-thio-2,4-oxazolidinedione

(*c*) 5-[(3-ethyl-2-benzothiazolinylidene)ethylidene]-3-heptyl-1-phenyl-2-thiohydantoin

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

(*e*) 5-[(3-ethyl-2-benzothiazolinylidene)ethylidene]-2-thiohydantoin

Example 2

Several light-developable, direct-print, light-sensitive, gelatine-silver chlorobromide emulsions of the type described in Example 1 were prepared and exposed as described in Example 1 except that the dyes were utilized at a concentration of 133 mg. per mole of silver halide and the potassium iodide was utilized at a concentration of 0.83 gram per mole of silver halide. The results of the tests are summarized by the data set out in Table II below.

TABLE II

Dye	Visible 0.15 log E Steps On Exposure and Photodevelopment	
	Minus Blue	White
None	9	17
a	12	18
f	5	17
g	4	17
h	9	17
i	9	18
j	13	18

In Table II above, dye *a* is described in Example 1 and dyes *f* to *j* are identified below.

(*f*) 5-[(3-ethylnaphtha{2,1-d}oxazolin-2-ylidene)ethylidene]-3-n-heptyl-1-phenyl-2-thiohydantoin

(*g*) 5-[(3-ethyl-2-benzoxazolinylidene)ethylidene]4-thiohydantoin

(*h*) 3-ethyl-5-[(3-ethyl-2-benzothiazolinylidene)ethylidene]-2-thiohydantoin

(*i*) 5-[di(3-ethyl-2-benzothiazolinylidene)isopropylidene]-1-methyl-2-thiobarbituric acid

(*j*) 5-[di(3-ethyl-2-benzothiazolinylidene)isopropylidene]-2-thiobarbituric acid.

Example 3

Several light-developable, direct-print, light-sensitive, gelatine-silver chlorobromide emulsions of the type described in Example 1 were prepared and exposed as described in Example 1 except that various thiourea halogen acceptors were substituted for the 1-n-butyl-1,2,5,6-tetrahydro-1,3,5-triazine-4-thiol halogen acceptor. Dye *d* described in Example 1 was utilized at a concentration of 120 mg. per mole of silver halide as the optical sensitizing dye, the various halogen acceptors were used at a concentration of 0.12 mole percent based on the silver halide and the potassium iodide was utilized at a concentration of 1.65 grams per mole of silver halide. The various coatings were exposed as described in Example 1. Results of the tests are summarized by the data set out in Table III below. In addition to the tests described in Example 1, other test portions were exposed to D_{max} and the whole strip photodeveloped 5 minutes with a 60 foot-candle cool white fluorescent light. The density in the exposed and unexposed areas was read through a Wratten No. 15 Filter on a curve-tracing densitometer and the difference recorded as ΔD for 300 foot-candle-minutes (f.c.m.) of photodevelopment. This latter determined value is also set out in Table III below.

TABLE III

Thiourea Compound	Visible 0.15 log E Steps On Exposure and Photodevelopment		300 f.c.m. ΔD
	Minus Blue	White	
I	15	21	.38
II	14	21	.37
III	14	21	.37
IV	15	21	.36

The designated thiourea compounds of Table III above are identified below.

(I) 2-imidazolinethione

(II) 1-methyl-2-imidazolethione

(III) 1-methyl-2-imidazolinethione

(IV) 1,3-dimethyl-2-imidazolinethione

Example 4

A light-developable, direct-print, light-sensitive gelatine-silver chlorobromide emulsion (95% bromide, 5% chloride) was prepared by the general method as described in Example 1. To various samples of the emul-

sion were added various sensitizing dyes at a concentration of 120 mg. of dye per mole of silver halide, 1.66 grams of potassium iodide per mole of silver halide, and a thiourea halogen acceptor at a concentration of 400 mg. per mole of silver halide. The various emulsions were coated at a coverage of 258 mg. of silver per square foot and 560 mg. of gelatin per square foot on photographic paper supports. The various coatings were thereafter exposed as described in Example 3 and the number of visible 0.15 log E steps obtained when exposed through a yellow filter were observed as well as the differences in density between the D_{max} and D_{min} areas and the amount of residual dye stain after photodevelopment were observed and recorded in Table IV below.

TABLE IV

	Thiourea Compound	Dye	Visible 0.15 log E Steps On Exposure and Photodevelopment	300 f.c.m. ΔD	Dye Stain
			Minus Blue		
V		None	0	.38	
V		*m*	10	.35	Low.
V		*l*	10	.36	Low.
V		*d*	7	.43	Low.
V		*k*	3	.42	Low.
VI		None	0	.39	
VI		*m*	13	.40	Low.
VI		*l*	13	.40	Low.
VI		*d*	13	.39	Low.

In Table IV, the dyes not previously identified in other examples hereinbefore are:

(*k*) 3-n-heptyl-5-[(3 - methyl - 2 - thiazolidinylidene) ethylidene]rhodanine

(*l*) 5 - [(3 - ethyl - 2 - benzothiazolidinylidene)ethylidene)rhodanine

(*m*) 5-[(3 - ethyl - 2 - benzothiazolinylidene)ethylidene]-2-thio-2,4-oxazolidinedione

In Table IV the thiourea compounds are:

(V) 1-n-butyl-1,2,5,6-tetrahydro-1,3,5-triazine - 4 - thiol

(VI) Thiourea

Example 5

A light-developable, direct-print, light-sensitive large-grain gelatine-silver chlorobromoiodide emulsion (95.21 mole percent bromide, 4.5 mole percent chloride, 0.34 mole percent iodide) having silver halide grains of high-internal sensitivity was prepared by slowly adding an aqueous solution of silver nitrate to an agitated gelatin solution of potassium bromide, potassium chloride and potassium iodide at 71° C., this emulsion being denominated "Emulsion A." A second emulsion, similar to Emulsion A, was prepared except 0.85 gram of lead nitrate per mole of silver was added to the silver nitrate in order to form silver halide crystals containing lead ions, this second emulsion being denominated "Emulsion B." Emulsion A was coated with and without 0.85 gram of lead nitrate per mole of silver halide added to the coating melt just prior to coating. Emulsion B was coated without any additional lead nitrate added. Also, dye *n*, 3-ethyl-5-(1 - ethyl - 2 - β - naphthothiazylidene-isopropylidene)-rhodanine, at a concentration of 120 mg. per mole of silver was added to the coatings as summarized in Table V below. All of the coatings were made on photographic paper supports at coverages of 256 mg. of silver per square foot and 558 mg. of gelatin per square foot. The coatings were exposed on an Edgerton, Germeshausen and Grier Mark VI sensitometer containing a xenon flash lamp for 10^{-4} seconds through a 0.15 log E density-increment neutral density step tablet to white light and through a Wratten No. 15 (minus blue) filter. The exposed photographic elements were photodeveloped by exposure to 50 foot-candles of cool white fluorescent light for 5 minutes. The results are summarized in Table V below.

TABLE V

	Emulsion and Addenda	D_{min}	Visible 0.15 log E Steps on Exposure and Photodevelopment	
			Minus Blue	White
1	Emulsion A	.06	0	4
2	Emulsion A plus lead nitrate in melt	.06	0	5
3	Emulsion B [1]	.06	0	5
4	Emulsion A plus Dye *n*	.36	14	17
5	Emulsion A plus lead nitrate plus Dye *n*	.36	14+	17
6	Emulsion B [1] plus Dye *n*	.31	15−	17

[1] Lead nitrate added during precipitation of the silver halide.

As can be observed from the data set out in Table V, emulsions with silver halide grains formed in the presence of a water-soluble lead salt, as was the case with Emulsion B, cooperate with spectral sensitizing dyes to result in direct-print images having lower D_{min} or density in background areas than result with comparable emulsions wherein the water-soluble lead salt is added to the emulsion just prior to coating. Further, such a reduced D_{min} is obtained without adversely affecting the speed of the emulsion to white and minus blue light. Results illustrating synergism of the type set out in Table V were also obtained with dye *c* described above, as well as with dye *n*, dye *o*, dye *p*, dye *q* and dye *r* identified below, at concentrations of 120 mg. of dye per mole of silver in Emulsion B.

Dye *n*: 3-ethyl-5-(1-ethyl-2-β-naphthothiazylidene - isopropylidene)rhodanine

Dye *o*: 3-ethyl-5-(3-ethyl-2-benzothiazolylidene - isopropylidene)-2-thio-2,4-oxazolidenedione

Dye *p*: 3,3'-diethyl-9-methyl-5,5'-diphenyloxacarbocyanine bromide

Dye *q*: 3,3'-diethyl-9-methyl-thiacarbocyanine bromide

Dye *r*: 3-methyl-1'-ethylthia-2'-cyanine iodide

Example 6

Several light-developable, direct-print, light-sensitive silver halide emulsions of the invention containing halogen acceptors were prepared and coated. To several portions of "Emulsion B" described in Example 5 were added various spectral sensitizing dyes and halogen acceptors as described in Table VI, and thereafter coated and exposed as described in Example 5. In Table VI, the halogen acceptor, dithiourea, is designated as "DTB" and was coated at a concentration of 0.45 g. per mole of silver, the halogen acceptor, imidazoline-2-thione (also called ethylenethiourea), is designated as "ETU" and was coated at a concentration of 0.236 g. per mole of silver, and potassium iodide is designated as "KI" and was coated at a concentration of 1.65 g. per mole of silver.

TABLE VI

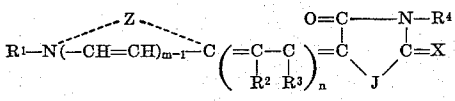
	Addenda in Emulsion B *	D_{min}	D_{max}	Visible 0.15 log E Steps on Exposure and Photodevelopment	
				Minus Blue	White
1	None	.06	.06	0	4
2	Dye *c* plus DTB	.61	.31	13	17
3	Dye *n* plus DTB	.59	.33	15−	18
4	Dye *o* plus DTB	.59	.32	14	18
5	Dye *p* plus DTB	.60	.36	12	16
6	Dye *q* plus DTB	.60	.35	13	17
7	Dye *r* plus DTB	.57	.30	7	16
8	Dye *c* plus ETU plus KI	.56	.31	9+	16
9	Dye *n* plus ETU plus KI	.59	.35	13	17
10	Dye *o* plus ETU plus KI	.54	.28	6	16
11	Dye *p* plus ETU plus KI	.57	.30	10−	17
12	Dye *q* plus ETU plus KI	.61	.37	14	18

The present invention thus provides new useful light-developable, direct-print, light-sensitive silver halide emulsions.

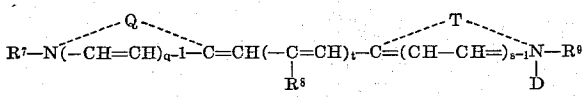
The invention has been described in considerable detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

I claim:

1. A light-developable, direct-print silver halide emulsion sensitized with a spectral sensitizing dye and wherein the silver halide grains of said emulsion are formed in the presence of lead ions, said spectral sensitizing dye having a formula selected from the group consisting of



and



wherein:

(A) R^1, R^7 and R^9 are each selected from the group consisting of
  (1) an alkyl radical, and
  (2) an aryl radical;

(B) R^2, R^3, R^4 and R^8 are each selected from the group consisting of
  (1) an alkyl radical,
  (2) an aryl radical, and
  (3) a hydrogen atom;

(C) J 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^5 can be any of the substituents of R^4, and

  (5) a group having the formula



wherein R^6 can be any of the substituents of R^4;

(D) Q, T and Z each represent the atoms required to complete a basic heterocyclic nucleus, Z being other than the atoms required to complete a thiazoline group when J is a sulfur atom;

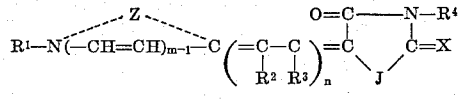
(E) *m*, *q* and *s* are each positive integers of 1 to 2;

(F) *n* and *t* are each positive integers of 0 to 2;

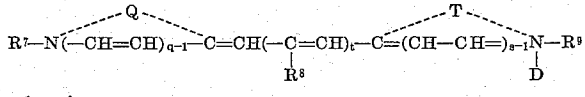
(G) D is an acid anion; and

(H) X is selected from the group consisting of a sulfur atom and a selenium atom.

2. A light-developable, direct-print silver halide emulsion wherein the silver halide forms latent images predominantly inside the silver halide grains, said silver halide grains having been formed in the presence of about .01 to 5 mole percent of lead ions based on the silver, and said silver halide emulsion being spectrally sensitized with a spectral sensitizing dye having a formula selected from the group consisting of



and



wherein:

(A) R^1, R^7 and R^9 are each selected from the group consisting of
  (1) an alkyl radical, and
  (2) an aryl radical;

(B) R^2, R^3, R^4 and R^8 are each selected from the group consisting of
  (1) an alkyl radical,
  (2) an aryl radical, and
  (3) a hydrogen atom;

(C) J 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^5 can be any of the substituents of R^4, and

  (5) a group having the formula



wherein R^6 can be any of the substituents of R^4;

(D) Q, T and Z each represent the atoms required to complete a basic heterocyclic nucleus, Z being other than the atoms required to complete a thiazoline group when J is a sulfur atom;

(E) *m*, *q* and *s* are each positive integers of 1 to 2;

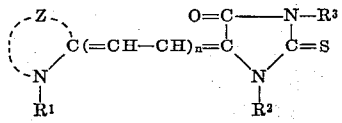
(F) *n* and *t* are each positive integers of 0 to 2;

(G) D is an acid anion; and

(H) X is selected from the group consisting of a sulfur atom and a selenium atom.

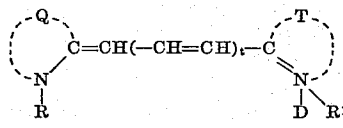
3. A light-developable, direct-print silver halide emulsion wherein the silver halide forms latent images pre-

dominantly inside the silver halide grains, said silver halide grains having been formed in the presence of about .01 to 5 mole percent of lead ions based on the silver, and said silver halide emulsion being spectrally sensitized with a spectral sensitizing dye having the formula



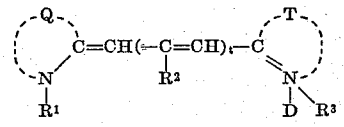
wherein R^1 and R^3 are each alkyl radicals; R^2 is a phenyl radical; n is a positive integer of 0 to 2; and Z represents the atoms required to complete a 5 to 6 membered basic heterocyclic nucleus.

4. A light-developable, direct-print silver halide emulsion wherein the silver halide forms latent images predominantly inside the silver halide grains, said silver halide grains having been formed in the presence of about .01 to 5 mole percent of lead ions based on the silver, and said silver halide emulsion being spectrally sensitized with a spectral sensitizing dye having the formula



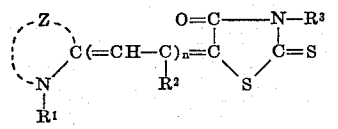
wherein R and R^1 are each alkyl radicals; t is a positive integer of 0 to 2; D is an acid anion; and Q and T each represent the atoms required to complete a 5 to 6 membered basic heterocyclic nucleus.

5. A light-developable, direct-print silver halide emulsion wherein the silver halide forms latent images predominantly inside the silver halide grains, said silver halide grains having been formed in the presence of about .01 to 5 mole percent of lead ions based on the silver, and said silver halide emulsion being spectrally sensitized with a spectral sensitizing dye having the formula



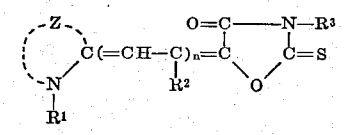
wherein R^1, R^2 and R^3 are each alkyl radicals; t is a positive integer of 0 to 2; D is an acid anion; and Q and T each represent the atoms required to complete a 5 to 6 membered basic heterocyclic nucleus.

6. A light-developable, direct-print silver halide emulsion wherein the silver halide forms latent images predominantly inside the silver halide grains, said silver halide grains having been formed in the presence of about .01 to 5 mole percent of lead ions based on the silver, and said silver halide emulsion being spectrally sensitized with a spectral sensitizing dye having the formula



wherein R^1, R^2 and R^3 are each alkyl radicals; n is a positive integer of 0 to 2; and Z represents the atoms required to complete a 5 to 6 membered basic heterocyclic nucleus other than a thiazoline group.

7. A light-developable, direct-print silver halide emulsion wherein the silver halide forms latent images predominantly inside the silver halide grains, said silver halide grains having been formed in the presence of about .01 to 5 mole percent of lead ions based on the silver, and said silver halide emulsion being spectrally sensitized with a spectral sensitizing dye having the formula



wherein R^1, R^2 and R^3 are each alkyl radicals; n is a positive integer of 0 to 2; and Z represents the atoms required to complete a 5 to 6 membered basic heterocyclic nucleus.

8. A light-developable, direct-print, gelatino silver halide emulsion wherein the silver halide forms latent images predominantly inside the silver halide grains, said silver halide grains having been formed in the presence of about .01 to 5 mole percent of lead ions based on the silver halide, and said silver halide emulsion being spectrally sensitized with about 10 to 1000 mg. per mole of said silver halide of 5-[(3-ethyl-2-benzothiazolinylidene)ethylene] rhodanine.

9. A light-developable, direct-print gelatino silver halide emulsion wherein the silver halide forms latent images predominantly inside the silver halide grains, said silver halide grains having been formed in the presence of about .01 to 5 mole percent of lead ions based on the silver halide, and said silver halide emulsion being spectrally sensitized with about 10 to 1000 mg. per mole of said silver halide of 5-[(3-ethyl-2-benzothiazolinylidene)ethylidene]-3-heptyl-1-phenyl-2-thiohydantoin.

10. A light-developable, direct-print gelatino silver halide emulsion wherein the silver halide forms latent images predominantly inside the silver halide grains, said silver halide grains having been formed in the presence of about .01 to 5 mole percent of lead ions based on the silver halide, and said silver halide emulsion being spectrally sensitized with about 10 to 1000 mg. per mole of said silver halide of 5-[(1-ethylnaphtho{1,2-d}thiazolin-2-ylidene)ethylidene]-3-heptyl-1-phenyl-2-thiohydantoin.

11. A light-developable, direct-print gelatino silver halide emulsion wherein the silver halide forms latent images predominantly inside the silver halide grains, said silver halide grains having been formed in the presence of about .01 to 5 mole percent of lead ions based on the silver halide, and said silver halide emulsion being spectrally sensitized with about 10 to 1000 mg. per mole of said silver halide of 3,3'-diethyl-9-methylthiacarbocyanine bromide.

12. A light-developable, direct-print gelatino silver halide emulsion wherein the silver halide forms latent images predominantly inside the silver halide grains, said silver halide grains having been formed in the presence of about .01 to 5 mole percent of lead ions based on the silver halide, and said silver halide emulsion being spectrally sensitized with about 10 to 1000 mg. per mole of said silver halide of 3-methyl-1'-ethylthia-2'-cyanine iodide.

13. A light-developable, direct-print silver halide emulsion as described in claim **1** wherein the halide of the silver halide is predominantly bromide.

14. A light-developable, direct-print silver halide emulsion as described in claim **1** prepared with an organic thioether silver halide solvent present during the grain growth of the silver halide.

15. A light-developable, direct-print gelatino silver halide emulsion wherein the silver halide forms latent images predominantly inside the silver halide grains, said silver halide grains having been formed in the presence of about .01 to 5 mole percent of lead ions based on the silver halide, and said silver halide emulsion being spectrally sensitized with about 10 to 1000 mg. per mole of

said silver halide of 3-ethyl-5-[(1-ethyl-2-β-naphthothiazylidene)isopropylidene]rhodanine.

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NORMAN G. TORCHIN, *Primary Examiner.*

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,287,136 November 22, 1966

Clarence E. McBride

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 3, in the table before the second column insert -- G. --, as a heading; line 29, before "as" insert -- zein --; column 4, line 8, for "hetercyclic" read -- heterocyclic --; column 6, line 45, for "5,5" read -- 5,5' --; column 10, TABLE II, second column, line 1 thereof, for "9" read -- 0 --; column 13, TABLE VI, heading to third column, for "Dmin" read -- Dmax --; same column, TABLE VI, heading to fourth column, for "Dmax" read -- Dmin --.

Signed and sealed this 12th day of September 1967.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents