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3,287,137
LIGHT-DEVELOPABLE SILVER HALIDE
EMULSIONS

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This application is a continuation-in-part of my copending application, U.S. Serial No. 222,964, filed September 11, 1962, now abandoned and my copending application, U.S. Serial No. 394,062, filed September 2, 1964.

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 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 stable 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 hydrophilic colloid-silver halide emulsion layer which, when exposed to a high intensity source of electromagnetic radiation, forms a latent image which can then be developed by subsequent general exposure to a second source of radiation of lower intensity. Such direct-writing or direct-print emulsions are faster than print-out emulsions and require no chemical development. However, many of the recording papers of this third type have a slow rate of photodevelopment and the background areas tend to build up to obscure the image on subsequent exposure to light.

It is an object of this invention to provide a new class of light-developable, direct-print, radiation-sensitive silver halide emulsions.

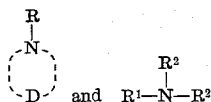
It is another object of this invention to provide novel photographic silver halide emulsions suitable for preparing direct-print recording photographic elements that can be exposed to a high intensity trace and thereafter photo-developed to produce images particularly characterized as having low D_{min} or background density.

It is still another object of this invention to provide new photodevelopable photographic silver halide emulsions that are characterized as having high 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 containing novel cooperating or synergistic addenda for such emulsions.

These and other objects of the invention are accomplished with a light-developable, direct-print silver halide emulsion containing a nitrogen-containing halogen acceptor and wherein the silver halide grains of the emulsion are formed in the presence of lead ions.

The nitrogen-containing halogen acceptors used in the emulsions of the invention can be represented by the formulas,



wherein: R, R¹ and R³ can each be hydrogen atoms, alkyl

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radicals, aryl radicals, including substituted alkyl and aryl radicals, or acyl radicals (e.g.,



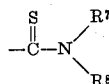
wherein R⁴ is a hydrogen atom, an alkyl radical or an aryl radical); R² can be a nitrogen-containing radical such as an amino radical or a thiocarbamyl radical, including substituted amino and thiocarbamyl radicals; and D represents the necessary atoms to complete a heterocyclic nucleus generally having 5 or 6 atoms including at least two nitrogen atoms and at least one divalent radical having the formula,



wherein X can be a sulfur atom, an oxygen atom, a selenium atom or an imino radical ($=\text{NH}$). When a nitrogen atom comprising D or R² is attached directly to the nitrogen atoms of the above formulas, at least one hydrogen atom is attached to at least one of such nitrogen atoms of the halogen acceptor. The amino radical for substituent R² can be represented by the formula,



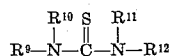
wherein R⁵ and R⁶ can each typically be such substituents as hydrogen atoms, alkyl radicals, aryl radicals or acyl radicals as described above for R¹ and R³. The thiocarbamyl radical for substituent R² can be represented by the formula,



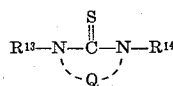
wherein R⁷ and R⁸ can be the same substituents as R⁵ and R⁶ or amino radicals.

Particularly useful nitrogen-containing halogen acceptors used in the emulsions of the invention can be further represented by the following subgeneric formulas:

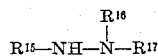
Formula A



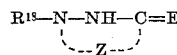
Formula B



Formula C



Formula D



wherein: R⁹, R¹⁰, R¹¹, R¹², R¹³, R¹⁴, R¹⁵, R¹⁶, R¹⁷ and R¹⁸ can each be hydrogen atoms, alkyl radicals, aryl radicals or acyl radicals as described above for R¹ and R³; E can be

a sulfur atom, an oxygen atom, a selenium atom or an imino radical; and Q and Z can be the necessary atoms to complete a heterocyclic nucleus generally having 5 or 6 members. Q and Z typically are the necessary atoms to complete such moieties as a triazole-thiol, a mercaptoimidazole, an imidazolidine-thione, a triazine-thiol, a thiobarbituric acid, a thiouracil, a urazole including a thiourazole and the like heterocyclic moieties.

With respect to the above formulas of nitrogen-containing halogen acceptors: the aryl radical substituents are those of the naphthyl and phenyl series, and include such common substituents as alkyl groups, halogen atoms, acyl radicals and the like; the alkyl radical substituents typically can contain 1 to 20 carbon atoms and more generally 1 to 8 carbon atoms, and can be substituted with such radicals as aryl radicals, halogen atoms, acyl radicals and the like.

Typical halogen acceptors of the thiourea type represented by Formula A and Formula B are disclosed in copending Kitz application, U.S. Serial No. 303,146 filed August 19, 1963, now U.S. Patent No. 3,241,971; and in copending Fix application, U.S. Serial No. 338,605, filed January 20, 1964. Typical halogen acceptors of the hydrazine type represented by Formula C are disclosed in Ives, U.S. Patent 2,588,982, issued March 11, 1952. Typical halogen acceptors of the type represented by Formula D are the urazole and thiourazole halogen acceptors disclosed in Bacon and Illingsworth application, titled "Light-Developable Direct-Print Silver Halide Emulsions," which was filed concurrently herewith.

Examples of specific nitrogen-containing halogen acceptors are set out below.

1,3-dimethyl-2-imidazolidinethione
2-imidazolidinethione
1-phenyl-5-mercaptopotetrazole
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-mercaptoimidazole
1-phenyl-2-imidazolidinethione
4,5-diphenyl-4-imidazolidine-2-thione
1-methyl-2-mercaptoimidazole
1-n-butyl-1,2,5,6-tetrahydro-1,3,5-triazine-4-thiol
Thiourea
1-methyl-2-imidazolidinethione
D-mannose thiosemicarbazone
Morpholino-2-propane thiosemicarbazone
D-galactose thiosemicarbazone
Urazole
3-thiourazole
3,5-dithiourazole
3,5-dithiourazole hydrazine salt
4-aminourazole hydrazine salt
3,5-dithiourazole hydrazine salt
Urazole sodium salt
4-(1-naphthyl) urazole
4-ethylurazole
1-phenylurazole
4-phenylurazole
1-butylurazole
1-octylurazole
4-butyl-3,5-dithiourazole
1,4-diphenylurazole

1,4-dibutylurazole
1,4-dibutyl-3,5-dithiourazole
1,4-diphenyl-3,5-dithiourazole
1-ethyl-4-phenylurazole
1-ethyl-4-phenyl-3,5-dithiourazole
3-thio-5-iminourazole
5-selenourazole
Hydrazine
Phenylhydrazine hydrochloride
2,5-dichlorophenyl hydrazine
p-Tolylhydrazine hydrochloride
 α -Naphthylhydrazine
 α -Benzyl- α -phenylhydrazine
p-Toluene sulfonyl hydrazine
Hexylhydrazine

The concentrations of the described nitrogen-containing halogen acceptors utilized in the silver halide emulsions of the invention can be widely varied in accordance with usual practice. Generally, about .1 to 100 mole percent, and preferably about 1 to 50 mole percent, based on the silver halide in the emulsion of the nitrogen-containing halogen acceptor is utilized.

A wide variety of light-developable, direct-print, photographic silver halide emulsions can be utilized in the invention, such being well known to those skilled in the art. Suitable silver halides includes silver chloride, silver bromide, silver bromiodide, silver chloriodide, and silver chlorobromiodide. The preferred emulsions are those wherein the halide of the silver halide is 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 copending 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 my above-mentioned copending application 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 are 3,6-dithia-1,8-octanediol, 1,10-dithia-4,7,13,16-tetraoxacyclooctadecane, 7,10-dithia-1,16-dicarboxamido-3,14-dithiahexadecane-6,11-dione, and 1,17-di-(N-ethylcarbonyl)-6,12-dithia-9-oxaheptadecane. The amount of thioether utilized to prepare the silver halide emulsions described in my copending application 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 can be used in the invention, such having silver halide grains wherein a predominant amount of the sensitivity 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	39.6
Hydroquinone	6.0

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DEVELOPER A—Continued

	G.
Sodium carbonate, desiccated	18.7
Potassium bromide	0.86
Citric acid	0.68
Potassium metabisulfite	1.5
Water to make 1 liter	

DEVELOPER B

	G.
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 to 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 Yutzky, 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; zein 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. Mixtures of such organic colloids can also be used.

Although silver halide emulsions are generally made with an equivalent or slight excess of halide ion present, I have found it desirable to add additional water-soluble iodide to the silver halide emulsion after its precipitation but before it is coated. More generally, about .1 to 50 mole percent, and preferably about 1 to 10 mole percent of water-soluble iodide based on the silver halide in the emulsion is used. Illustrative water-soluble iodides include ammonium, calcium, lithium, magnesium, potassium, or sodium iodide.

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. 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 halide. 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.

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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, as well as spectral sensitizing dyes of the type described in copending Jones application, U.S. Serial No. 380,044, filed July 2, 1964.

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, glass, cellulose nitrate film, cellulose acetate film, polyvinyl acetal film, polystyrene film, polyethyleneterephthalate film and related films of resinous materials and others.

In forming a photodeveloped image with a typical photographic element containing an emulsion of the invention, the photographic element is initially exposed to a relatively short duration and high intensity source of electromagnetic radiation (e.g., at least about .1 foot-candle second at an intensity of more than about 100 foot-candles) such as a high intensity light source rich in blue and ultraviolet light such as are used in oscillographs described in Heiland, U.S. Patent 2,580,427, issued January 1, 1952, high intensity visible light, X-radiation and the like, to form a latent image in the emulsion of the photographic element, and thereafter the resulting latent image is photodeveloped by overall exposure of the emulsion to a radiation source of lower intensity than the original exposure, such as to a conventional fluorescent light, light from incandescent lamps commonly used for general illumination, or even ordinary daylight. Generally, the latent image formed in the emulsion in the first instance is not visible and does not become visible until photodevelopment. Heat is desirably utilized during the photodevelopment step. Typically the subject emulsions are heated to a temperature of about 90° C. to 200° C. for about 1 to 30 seconds and photodeveloped after the initial high intensity exposure.

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

Example 1

A light-developable, direct-print, large-grain gelatin-silver chlorobromide emulsion (95 mole percent bromide, 5 mole percent chloride) having silver halide grains of high internal sensitivity was prepared by slowly adding a aqueous solution of silver nitrate containing .85 g. of lead nitrate per mole of silver to an agitated gelatin solution containing a stoichiometric excess of potassium chloride and potassium bromide, .5 g. of a thioether silver halide solvent of the type described in my said application Serial No. 222,964 per mole of silver halide 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 of such portions of emulsion was added a nitrogen-containing halogen acceptor as indicated in Table I below. The resulting emulsions were coated on paper supports at a silver coverage of 258 mg. per square foot and at a gelatin coverage of 565 mg. per square foot. Strips of each coating containing various halogen acceptors, as well as a corresponding strip containing no halogen acceptor, were image-exposed, wherein the image constituted opaque bars with a high intensity xenon lamp (Heiland Strobosonar 100 watt-second xenon lamp for about .002 second at a distance of about 8 feet) and photodeveloped for 5 minutes with a 60 foot-candle cool white fluorescent light. Table I below summarizes the densities of the image or exposure areas ($D_{max.}$), the densities of the background or unexposed areas ($D_{min.}$) and the density differences between such areas (ΔD) for each of the coatings. The concentration of halogen acceptor indicated in Table I is in mole percent based on the silver halide in the emulsion.

TABLE I

Nitrogen-Containing Halogen Acceptor	D _{max}	D _{min}	ΔD
None	.21	.13	.08
Urazole, 16% mole percent	.56	.18	.38
3-thiourazole, 5 mole percent	.58	.18	.40
3,5-dithiourazole, 5 mole percent	.61	.18	.43
3,5-dithiourazole hydrazine salt, 4 mole percent	.70	.21	.49
4-ethylurazole, 15 mole percent	.43	.14	.29
1-phenylurazole, 15 mole percent	.36	.13	.23
4-phenylurazole, 15 mole percent	.38	.13	.25
4-aminourazole hydrazine salt, 5 mole percent	.61	.17	.44
3-thio-5-iminourazole, 4.7 mole percent	.57	.17	.40
Hydrazine hydrochloride, 5 mole percent	.51	.16	.35
Hydrazine hydrochloride, 12 mole percent	.60	.18	.42
Carbohydrazide, 10 mole percent	.61	.18	.43
Dithiobiurea, 1 mole percent	.61	.17	.44

As can be observed from the data set out in the table above, light-developable, direct-print silver halide emulsions containing a wide variety of halogen acceptors can be utilized to improve the utility of silver halide emulsions wherein lead ions are present during the formation of the silver halide grains. If desired, the exposed coatings can be chemically developed and fixed to form archival quality images, a 1 minute development and a 1.5 minute fix at 72° F. in the following baths being suitable:

DEVELOPING COMPOSITION

N-Methyl-p-aminophenol sulfate	g.	3.0
Sodium sulfite (anhydrous)	g.	45.0
Hydroquinone	g.	12.0
Sodium carbonate monohydrate	g.	80.0
Potassium bromide	g.	2.0
Sodium thiosulfate	g.	5.0
Benzoxazolethiole	g.	25.0
Water to make 2 liters.		

FIXING COMPOSITION

Sodium thiosulfate	g.	240.0
Sodium sulfite (anhydrous)	g.	15.0
Acetic acid, 28%	cc.	48.0
Boric acid	g.	7.5
Potassium alum	g.	15.0
Water to make one liter.		

Example 2

A sample of the light-developable, direct-print silver halide emulsion containing 4.7 mole percent of 3-iminothiourazole and coated on a paper support as described in Example 1 was incubated at 120° F. and 35% relative humidity for 7 days prior to being exposed and photodeveloped as described in Example 1. The density of the resulting D_{max}, or image area was .53 and the density of the D_{min}, or background area was .15 and ΔD or D_{max}—D_{min} was .38.

Example 3

A light-developable, direct-print silver halide emulsion as described in Example 1 was prepared and coatings were prepared containing 5, 10 and 40 mole percent of urazole based on the silver halide. The coatings contained silver at a coverage of 258 mg. per square foot and gelatin at a coverage of 565 mg. per square foot. Each of the coatings 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. Good image discrimination of the magnitude illustrated by the data set out in the table above was obtained for each of the coatings after the exposure and photodevelopment.

Example 4

A light-developable, direct-print silver halide emulsion as described in Example 1 was prepared and coatings were prepared both with and without 5 mole percent of the

nitrogen-containing halogen acceptor, 3,5-dithiourazole hydrazine salt, as well as with a silver halide emulsion in which the silver halide was precipitated in the absence of lead nitrate. The various coatings were then exposed and photodeveloped as described in Example 1. The D_{max} and D_{min} values were then determined for the respective coatings, and which values are summarized in Table II below.

TABLE II

Feature Addenda	D _{max}	D _{min}	ΔD
(a) None	(1)	(1)	(1)
(b) Lead nitrate, .85 g./mole silver halide	.21	.13	.08
(c) 3,5-Dithiourazole hydrazine salt, 5 mole percent	.57	.39	.18
(d) (b)+(c)	.59	.17	.42

¹ No image.

As can be observed from the data summarized in Table II, nitrogen-containing halogen acceptors cooperate synergistically with the feature of forming the silver halide in the presence of lead ions in light-developable, direct-print silver halide emulsions. Coating (d) of the invention exhibited a desirably low background density (D_{min}) and a high degree of image discrimination (ΔD).

Example 5

A light-developable, direct-print, light-sensitive large-grain gelatin-silver chlorobromiodide 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, coatings of Emulsions A and B contained the nitrogen-containing halogen acceptor, imidazolidine-2-thione, at concentrations of .236 g. per mole of silver halide in the emulsions. The coatings also each contained 1.65 g. of potassium iodide per mole of silver halide in the emulsions. 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 to a xenon flash lamp and photodeveloped as described in Example 3. The results are summarized by the data set out in Table III below.

TABLE III

Emulsion and Addenda	D _{max}	D _{min}	ΔD
(1) Emulsion A	.47	.27	.20
(2) Emulsion A+lead nitrate in melt	.51	.28	.23
(3) Emulsion B ¹	.45	.22	.23
(4) Emulsion A+ETU ²	.58	.35	.23
(5) Emulsion A+lead nitrate in melt+ETU	.59	.35	.24
(6) Emulsion B+ETU	.55	.26	.29

¹ Lead nitrate added during precipitation of the silver halide.

² Imidazolidine-2-thione ("ethylenethiourea").

As can be observed from the data set out in Table III, emulsions with silver halide grains formed in the presence of a water-soluble lead salt, as was the case with Emulsion B, cooperate with the nitrogen-containing halogen acceptor to result in direct-print images having lower D_{min}, or density in background areas and better image discrimination (D_{max}—D_{min}, or ΔD) than result with comparable emulsions wherein the water-soluble lead salt is added to the emulsion just prior to coating. Similar

results are obtained if .45 g. of dithiobiurea per mole of silver halide in the emulsion were substituted for the imidazolidine-2-thione.

Example 6

A large-grain gelatin-silver chlorobromide light-developable direct-print emulsion (95% bromide, 5% chloride) having high internal sensitivity and low surface 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, .5 g. of a thioether silver halide solvent of the type described in my said application Serial No. 222,964, per mole of silver halide being added during the resulting precipitation. The emulsion was washed with water to remove water-soluble salts. To separate portions of this emulsion were added typical feature nitrogen-containing halogen acceptors as described in Table IV below and coated on paper supports at coverages of 258 mg. of silver per square foot and 560 mg. of gelatin per square foot. The coatings were exposed to a 100-microsecond flash on an Edgerton, Germeshausen and Grier Mark VI sensitometer containing a xenon light source through a 0.15 log E neutral density step tablet and thereafter photodeveloped for 5 minutes with a 60 foot-candle, cool-white fluorescent light source. The number of visible 0.15 log E steps obtained for the various coatings is summarized in Table IV. Also, the density difference between image and background after the 5 minute photodevelopment was observed for the various coatings, and which density differences are recorded in Table IV as "ΔD." In the various coatings the potassium iodide ("KI") was used at concentrations of 2.1 mole percent based on the silver halide and the nitrogen-containing halogen acceptors were used at concentrations of 3.7 mole percent based on the silver halide unless otherwise indicated.

TABLE IV

Emulsion Addenda	Visible 0.15 log E Steps on Exposure and Photodevelopment	ΔD
(1) KI	15	.37
(2) 1-n-butyl-1,2,5,6-tetrahydro-1,3,5-triazine-4-thiol	16	.28
(3) 1-n-butyl-1,2,5,6-tetrahydro-1,3,5-triazine-4-thiol+KI	17	.48
(4) 1-n-butyl-1,2,5,6-tetrahydro-1,3,5-triazine-4-thiol (5.8 mole percent)	16	.28
(5) Tetramethylthiourea+KI	16+	.36
(6) 1,3-dimethyl-2-imidazolinethione+KI	17	.45
(7) 3,4-diphenyl-5-mercapto-1,2,4-triazole+KI	15	.41
(8) 4-phenyl-3-mercapto-1,2,4-triazole+KI	16+	.39
(9) 2-mercaptoimidazole+KI	16+	.41
(10) 1-methyl-2-mercaptoimidazole+KI	16+	.40
(11) 2-mercaptoimidazoline+KI	17	.42
(12) 1-phenyl-2-mercaptoimidazoline+KI	16+	.42
(13) 1,3-dimethyl-2-mercaptoimidazoline+KI	16+	.39
(14) 5,5-dimethyl-2-mercaptohydantoin+KI	15	.39
(15) 4,5-diphenyl-2-mercaptoimidazoline+KI	16+	.40
(16) 1,1-diphenyl-2-thiourea+KI	15+	.43
(17) 1,3-di-(m-methoxyphenyl)-2-thiourea+KI	16	.41
(18) 1-(o-methoxyphenyl)-2-thiourea+KI	15+	.45
(19) 1-(p-methoxyphenyl)-2-thiourea+KI	16+	.45
(20) 1-methyl-1,2,5,6-tetrahydro-4-mercapto-1,3,5-triazine+KI	16+	.38
(21) 4-thiobarbituric acid+KI	15	.44
(22) 1-allyl-2-thiourea+KI	17	.44
(23) 2-thiouracil+KI	16	.38
(24) 1-acetyl-2-thiourea+KI	16+	.45
(25) 1-ethyl-1-(α-naphthyl)-2-thiourea+KI	16	.40
(26) 2-imidazolidinethione+KI	17	.47
(27) 1-isopentyl-2-thiourea+KI	17	.45
(28) 1-(2-diethylaminoethyl)-1,2,5,6-tetrahydro-4-mercapto-1,3,5-triazine+KI	17	.41
(29) 1,2-bis(1,2,5,6-tetrahydro-4-mercaptotriazine)-ethane+KI	17	.42
(30) 4-ethylcarboxymethyl-1,2,5,6-tetrahydro-4-mercapto-1,3,5-triazine+KI	17	.45
(31) 1-phenyl-2-thiourea+KI	17	.42
(32) Thiourea+KI	17	.44

As can be observed from the data set out in Table IV, a wide variety of nitrogen-containing halogen acceptors can

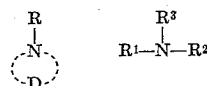
be utilized in the light-developable, direct-print lead-silver halide emulsions of the invention.

The silver halide of the emulsions of the invention described in the examples above were all formed or precipitated in the presence of lead ions in acidic media (about pH 2, sulfuric or nitric acid being utilized). The emulsions of the invention also all contained nitrogen-containing halogen acceptors. Such emulsions were demonstrated to be useful light-developable, direct-print 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 containing a nitrogen-containing halogen acceptor and wherein the silver halide grains of said emulsion have been formed in the presence of lead ions, said halogen acceptor having a formula selected from the group consisting of



wherein the substituents:

- (A) R, R¹ and R³ are each selected from the group consisting of a hydrogen atom, an alkyl radical, an aryl radical and an acyl radical;
 (B) R² is a nitrogen-containing radical selected from the group consisting of a thiocarbamyl radical and an amino radical; and
 (C) D represents the atoms necessary to complete a heterocyclic nucleus having 5 to 6 atoms including at least two nitrogen atoms and at least one divalent radical having the formula



wherein X is selected from the group consisting of and oxygen atom, a sulfur atom, a selenium atom and an imino radical;

except that when a nitrogen atom comprising one of said substituents is attached directly to a nitrogen atom of one of said formulas, the halogen acceptor contains at least one hydrogen atom attached to at least one of said nitrogen atoms.

2. A light-developable, direct-print silver halide emulsion wherein the silver halide grains have 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 contains a nitrogen-containing halogen acceptor having the formula



wherein D represents the atoms necessary to complete a heterocyclic nucleus having 5 to 6 atoms including at least one divalent radical having the formula



and at least two nitrogen atoms.

3. A light-developable, direct-print silver halide emulsion wherein the silver halide grains have 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 contains a nitrogen-containing halogen acceptor having the formula



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wherein D represents the atoms necessary to complete a heterocyclic nucleus having 5 to 6 atoms including at least one divalent radical having the formula



and at least two nitrogen atoms.

4. A light-developable, direct-print silver halide emulsion wherein the silver halide grains have 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 contains a nitrogen-containing halogen acceptor having the formula



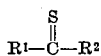
wherein R is an amino radical.

5. A light-developable, direct-print silver halide emulsion wherein the silver halide grains have 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 contains a nitrogen-containing halogen acceptor having the formula



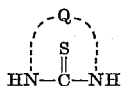
wherein R is a thiocarbamyl radical.

6. A light-developable, direct-print silver halide emulsion wherein the silver halide grains have 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 contains a nitrogen-containing halogen acceptor having the formula



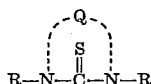
wherein R¹ and R² are each amino radicals.

7. A light-developable, direct-print silver halide emulsion wherein the silver halide grains have 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 contains a nitrogen-containing halogen acceptor having the formula



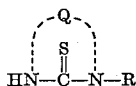
wherein Q represents the atoms necessary to complete a heterocyclic nucleus having 5 to 6 atoms.

8. A light-developable, direct-print silver halide emulsion wherein the silver halide grains have 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 contains a nitrogen-containing halogen acceptor having the formula



wherein Q represents the atoms necessary to complete a heterocyclic nucleus having 5 to 6 atoms and R is an alkyl radical.

9. A light-developable, direct-print silver halide emulsion wherein the silver halide grains have 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 contains a nitrogen-containing halogen acceptor having the formula



wherein Q represents the atoms necessary to complete a heterocyclic nucleus having 5 to 6 atoms and R is a phenyl radical.

10. A light-developable, direct-print silver halide emulsion wherein the silver halide grains have been formed

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in the presence of about .01 to 5 mole percent of lead ions based on the silver halide, and said silver halide emulsion contains a nitrogen-containing halogen acceptor having the formula

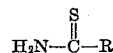


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10 wherein Q represents the atoms necessary to complete a heterocyclic nucleus having 5 to 6 atoms and R is an alkyl radical.

11. A light-developable, direct-print silver halide emulsion wherein the silver halide grains have 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 contains a nitrogen-containing halogen acceptor having the formula

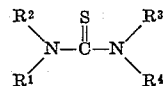
20



wherein R is an amino radical.

12. A light-developable, direct-print silver halide emulsion wherein the silver halide grains have 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 contains a nitrogen-containing halogen acceptor having the formula

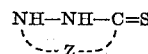
30



35 wherein R¹, R², R³ and R⁴ are each alkyl radicals.

13. A light-developable, direct-print silver halide emulsion wherein the silver halide grains have 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 contains a nitrogen-containing halogen acceptor having the formula

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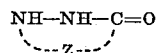


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wherein Z represents the atoms necessary to complete a thiourazole nucleus.

14. A light-developable, direct-print silver halide emulsion wherein the silver halide grains have 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 contains a nitrogen-containing halogen acceptor having the formula

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wherein Z represents the atoms necessary to complete a urazole nucleus.

15. A light-developable, direct-print silver halide emulsion wherein the silver halide grains have been formed in the presence of about .01 to 5 mole percent based on the silver halide of lead ions, said halide of said silver halide being predominantly bromide, and said silver halide emulsion contains about .1 to 100 mole percent based on said silver halide of 3,5-dithiourazole.

16. A light-developable, direct-print silver halide emulsion wherein the silver halide grains have been formed in the presence of about .01 to 5 mole percent based on the silver halide of lead ions, said halide of said silver halide being predominantly bromide, and said silver halide emulsion contains about .1 to 100 mole percent based on said silver halide of thiourea.

17. A light-developable, direct-print silver halide emulsion wherein the silver halide grains have been formed

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in the presence of about .01 to 5 mole percent based on the silver halide of lead ions, said halide of said silver halide being predominantly bromide, and said silver halide emulsion contains about .1 to 100 mole percent based on said silver halide of urazole.

18. A light-developable, direct-print silver halide emulsion wherein the silver halide grains have been formed in the presence of about .01 to 5 mole percent based on the silver halide of lead ions, said halide of said silver halide being predominantly bromide, and said silver halide emulsion contains about .1 to 100 mole percent based on said silver halide of imidazolidine-2-thione.

19. A light-developable, direct-print silver halide emulsion wherein the silver halide grains have been formed in the presence of about .01 to 5 mole percent based on the silver halide of lead ions, said halide of said silver

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halide being predominantly bromide, and said silver halide emulsion contains about .1 to 100 mole percent based on said silver halide of dithiobiurea.

References Cited by the Examiner

UNITED STATES PATENTS

2,596,742	5/1952	Vaughn et al.	96—107 X
2,717,833	9/1955	Wark	96—108
3,033,682	5/1962	Hunt	96—108
3,047,392	7/1962	Scott	96—108
3,123,474	3/1964	Byrne	96—94 X
3,148,987	9/1964	Willems	96—107 X

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,287,137

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 1, line 69, for $\begin{array}{c} R_2 \\ | \\ N \end{array}$ read -- $\begin{array}{c} R_3 \\ | \\ N \end{array}$ --; column 7, line 47, for "thiouradole" read -- thiourazole --.

Signed and sealed this 5th day of September 1967.

(SEAL)

Attest:

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Attesting Officer

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Commissioner of Patents