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3,271,157

LIGHT-DEVELOPABLE DIRECT-PRINT SILVER HALIDE EMULSIONS

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No Drawing. Continuation of abandoned application Ser. No. 222,964, Sept. 11, 1962. This application Apr. 29, 1965, Ser. No. 452,009

20 Claims. (Cl. 96—107)

This application is a continuing application of my co-pending application, Serial No. 222,964, filed September 11, 1962, now abandoned.

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

Radiation-sensitive photographic elements adapted for light recording, e.g., oscillographic recording, are known. Typical of such photographic elements are the developing-out and print-out type. The developing-out type of photographic element, as the name implies, requires that the exposed material be chemically developed and fixed in order to provide a stable visible image. The print-out type of photographic element 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 photographic element 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 photographic elements 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 having a high rate of photodevelopment.

It is another object of this invention to provide new light-developable 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 light-developable photographic silver halide emulsions that have high resistance in the initially unexposed areas to density increase upon photodevelopment and subsequent exposure to roomlight.

These and other objects of the invention are accomplished with light-developable, direct-print silver halide emulsions containing silver halide grains grown or formed in the presence of an organic thioether silver halide solvent.

Aqueous solutions of suitable organic thioether silver

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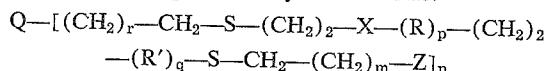
halide solvents utilized during the grain growth or formation of the silver halide grains of the present emulsions have a greater solubility for silver chloride than water. More specifically, such thioether silver halide solvents are those which, when utilized in aqueous solutions (60° C.) at 0.02 molar concentrations, are capable of dissolving more than twice the amount (by weight) of silver chloride than that which can be dissolved by water at 60° C.

The thioether silver halide solvent can be added to the silver halide emulsion at any stage of the preparation thereof before the silver halide grains have attained their ultimate size and shape, such as to the colloidal material in which the silver halide is precipitated, in combination with one of the water-soluble salts utilized to form the silver halide such as with the water-soluble silver salt (e.g., silver nitrate) or with a water-soluble halide such as an alkali metal halide, to the silver halide prior to or during the ripening of the silver halide, or during one or more of such emulsion preparation steps.

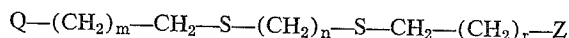
The amount of thioether silver halide solvent utilized can be widely varied depending on the effect desired, the nature of the thioether utilized and related variables. Concentrations of about .1 to 50 grams of thioether per mole of silver halide are suitably utilized, with about 1 to 10 grams of thioether per mole of silver halide being more generally utilized.

Typical organic thioether silver halide solvents that can be suitably utilized in preparing the emulsions of the invention contain at least one moiety wherein oxygen and sulfur atoms are separated by an ethylene radical (e.g., —O—CH₂CH₂—S—). Generally, the subject silver halide solvents have 1 to 3 thioether atoms (—S—) although silver halide solvents having more than 3 thioether atoms can be utilized.

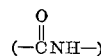
Certain of the present organic thioether silver halide solvents can be represented by the formulas:



and



wherein: r and m are integers of 0 to 4; n is an integer of 1 to 4; p and q are integers of 0 to 3; X is an oxygen atom (—O—), a sulfur atom (—S—), a carbamyl radical



a carbonyl radical



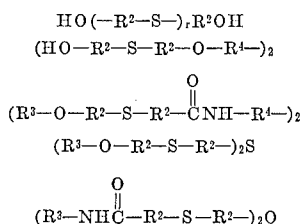
or a carboxy radical



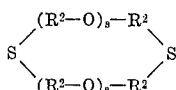
R and R' are ethylene oxide radicals (—O—CH₂CH₂—); Q and Z are hydroxy radicals (—OH), carboxy radicals, or alkoxy radicals (—O—alkyl) wherein the alkyl group has 1 to 5 carbon atoms; and Q and Z can also be substituents described for X linked to form a cyclic compound.

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Preferred organic thioether silver halide solvents suitable for forming the emulsions of the invention include compounds represented by the formulas:



and



wherein: r is an integer of 1 to 3; s is an integer of 1 to 2; R^2 is an alkylene radical having 1 to 5 carbon atoms and is preferably ethylene ($-\text{CH}_2\text{CH}_2-$); R^3 is an alkyl radical having 1 to 5 carbon atoms and is preferably ethyl; and R^4 is an alkylene radical having 1 to 5 carbon atoms and is preferably methylene ($-\text{CH}_2-$).

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 include silver chloride, silver bromide, silver bromoiodide, silver chloroiodide, and silver chlorobromoiodide. The preferred emulsions are those wherein the silver halide contains at least 50% bromide, less than 10% iodide and less than 50% chloride on a molar basis. For a description of suitable emulsions, reference is made to Davey et al., U.S. Patent 2,592,250, issued April 8, 1952; and Glafkides, Photographic Chemistry, vol. 1, pp. 31-2, Fountain Press, London.

The so-called "internal image" emulsions are particularly useful in the invention, such having silver halide grains wherein a predominant amount of the sensitivity is internal to the grains. Such internal image-forming 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
Sodium carbonate, desiccated -----	18.7
Potassium bromide -----	0.86
Citric acid -----	0.68
Potassium metabisulfite -----	1.5
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.	

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In preparing the present silver halide emulsions, the water-soluble silver salt and the water-soluble halide are reacted to precipitate the silver halide under acidic conditions. The pH of the silver halide precipitation is typically less than 6 and preferably less than 5. Such acids as phosphoric, trifluoroacetic, hydrobromic, hydrochloric, sulfur and nitric are typically utilized in the silver halide precipitating media to maintain acidic conditions. An excess of water-soluble halide is more generally used. The pAg during the silver halide precipitation is more generally about 8 to 10. The present silver halide emulsions can be washed after precipitation such as by the methods described in U.S. Patents 2,614,929 and 2,618,556. The silver halide grains of the emulsions of the invention generally have an average grain size of about .1 to 10 microns, and more generally about .5 to 2 microns, in diameter.

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 halide, particularly 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 halide based on the silver halide in the emulsion are present in the subject emulsions. Illustrative water-soluble halides include the ammonium, calcium, lithium, magnesium, potassium, and sodium salts.

Lead ions can be used in the precipitation or formation of the silver halide used in the emulsions of the invention. Water-soluble lead salts are typically added with a water-soluble silver salt to an appropriate water-soluble halide to precipitate a lead-silver halide. The amount of lead used in the present silver halide emulsions typically ranges from about .01 to 5 mole percent based on the silver. The use of such lead ions in the formation of the silver halide facilitates the reduction of background density ($D_{\min.}$) while exhibiting increased image density ($D_{\max.}$) when exposed to a high intensity light source and photodeveloped by exposure to a lower intensity light source.

Halogen acceptors of the type utilized in conventional light-developable, direct-print silver halide emulsions can be incorporated in the present emulsions. Typical halogen acceptors that can be utilized in the emulsions of the invention include stannous chloride, thiosalicylic acid, 1-phenyl-3-pyrazolidone, thiourea, thiosemicarbazide, 1-methyl-2-imidazolethione, 1-n-butyl-1,2,5,6-tetrahydro-1,3,5-triazine-4-thiol, D-mannose thiosemicarbazone, 1-phenyl-5-mercaptotetrazole, 4-thiobarbituric acid, urazole, 3-thiourazole, 1-phenylurazole, 4-ethylurazole, 3-imino-thiourazole and the like halogen acceptors.

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 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 of 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 con-

taining 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.

The silver halide emulsions of my invention can be spectrally sensitized with cyanine and merocyanine dyes, such as those 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); VanLare, U.S. Patent 2,739,149 (issued March 20, 1956); and Kodak Limited, British Patent 450,958, accepted July 15, 1936.

The emulsions of the invention can contain a suitable gelatin plasticizer such as glycerin; a dihydroxy alkane such as 1,5-pentane diol as described in Milton and Murray, U. S. Patent 2,960,404 (issued November 15, 1960); an ester of an ethylene bis-glycolic acid, such as ethylene bis(methyl glycolate) as described in Milton U.S. Patent 2,904,434 (issued September 15, 1959); bis(ethoxy diethylene glycol) succinate as described in Gray, U.S. Patent 2,940,854, issued June 14, 1960. The plasticizer can be added to the emulsion before or after the addition of a sensitizing dye, if used.

The emulsion can be hardened with any suitable hardener for gelatin as formaldehyde; a halogen-substituted aliphatic acid such as mucobromic acid as described in White, U.S. Patent 2,080,019 (issued May 11, 1937); a compound having a plurality of acid anhydride groups such as 7,8-diphenyl-bicyclo(2,2,2)-7-octene-2,3,5,6-tetracarboxylic dianhydride, or a dicarboxylic or a disulfonic acid chloride such as terephthaloyl chloride or naphthalene-1,5-disulfonyl chloride as described in Allen and Carroll, U.S. Patents 2,725,294 and 2,725,295 (both issued November 29, 1955); a cyclic 1,2-diketone such as cyclopentane-1,2-dione as described in Allen and Byers, U.S. Patent 2,725,305 (issued November 29, 1955); a bisester of methane-sulfonic acid, such as 1,2-di(methane-sulfonyl)ethane as described in Allen and Laakso, U.S. Patent 2,726,162 (issued December 6, 1955); 1,3-dihydroxy-methyl-benzimidazol-2-one as described in July, Knott and Pollak, U.S. Patent 2,732,316 (issued January 24, 1956); a dialdehyde or a sodium bisulfite derivative thereof, the aldehyde groups of which are separated by 2-3 carbon atoms, such as β -methyl-glutaraldehyde bis-sodium bisulfite; a bisaziridine carboxamide, such as trimethylene bis(1-aziridine carboxamide) as described in Allen and Webster, U.S. Patent 2,950,197 (issued August 23, 1960); or 2,3-dihydroxy dioxane as described in Jeffreys, U.S. Patent 2,870,013 (issued January 20, 1959).

The emulsions of the invention can contain a coating aid, such as saponin; a lauryl or oleoyl monoether of polyethylene glycol as described in Knox and Davis, U.S. Patent 2,831,766 (issued April 22, 1958); a salt of a sulfated and alkylated polyethylene glycol ether as described in Knox and Davis, U.S. Patent 2,719,087 (issued September 27, 1955); an acylated alkyl taurine, such as the sodium salt of N-oleoyl-N-methyltaurine as described in Knox, Twardokus, and Davis, U.S. Patent 2,739,891 (issued March 27, 1956); the reaction product of a dianhydride of tetracarboxybutane with an alcohol or an aliphatic amine containing from 8 to 18 carbon atoms which

is treated with a base, for example, the sodium salt of the monoester of tetracarboxybutane as described in Knox, Stenberg, and Wilson, U.S. Patent 2,843,487 (issued July 15, 1958); a water-soluble maleopimarate or a mixture of a water-soluble maleopimarate and substituted glutamate salt as described in Knox and Fowler, U.S. Patent 2,823,123 (issued February 11, 1958); an alkaline metal salt of a substituted amino acid, such as disodium N-(carbon-p-tert.octylphenoxy)pentaoxy) glutamate, or a sulfosuccinamate, such as tetrasodium N-(1,2-dicarboxyethyl)-N-octadecyl sulfosuccinamate, or N-lauryl disodium sulfosuccinamate.

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 glass, metals, paper, polyethylene-coated paper, polypropylene-coated paper, cellulose nitrate film, cellulose acetate film, polyvinyl acetal film, polystyrene film, polyethyleneterephthalate film and related films of resinous materials and others.

In forming a light-developed 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 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. 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. Thereafter the resulting latent image is photo-developed by overall exposure of the emulsion to a radiation source (e.g., at least about .0001 foot-candle second) 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.

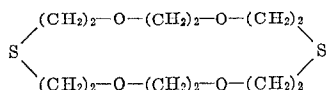
If desired, photographic elements containing the emulsions of the invention can be developed and fixed in aqueous chemical developing-out and fixing solutions after the initial exposure forming the latent image, or after the above-described photodevelopment, to make archival-quality records. Developing agents can be incorporated in the emulsions of the invention including such developing agents as hydroquinones, catechols, amino-phenols, 3-pyrazolidones and the like.

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

Example 1

A light-developable, direct-print, radiation-sensitive gelatin silver chlorobromiodide emulsion (91 mole percent bromide, 8.66 mole percent chloride and 0.34 mole percent iodide) having silver halide grains of high internal sensitivity was prepared by slowly adding an aqueous solution of silver nitrate containing 0.85 g. lead nitrate per mole of silver nitrate to an agitated aqueous solution of gelatin, potassium bromide, sodium chloride and potassium iodide at 71° C. at a pH of about 2.0 (adjusted with sulfuric acid). The resulting emulsion was designated "Emulsion A." Four additional emulsions were prepared in a similar manner but differing in that each of these emulsions contained a different level

of the thioether compound, 1,10-dithia-4,7,13,16-tetraoxycyclooctadecane,



in the aqueous gelatin-alkali metal halide solution before the addition of silver nitrate thereto. These emulsions were designated "Emulsions B, C, D, and E."

Emulsion	Concentration of Thioether (g./Ag mole)	Silver Halide Mean Grain Area
A-----	0	0.67 (S ²)
B-----	1	1.34
C-----	2	1.67
D-----	4	1.87
E-----	8	2.44

To each of these emulsions was added 2.2 grams per mole of silver of the halogen acceptor, thiosalicylic acid. The emulsions were then coated on a paper support at a silver coverage of 254 mg./ft.² and gelatin at a coverage of 560 mg./ft.². Samples of these coatings were exposed by covering one-half of the sample and then exposing the uncovered half to a flash from a Heiland-Strobnar-1 electronic flash unit having a color temperature of 7000° Kelvin (1/2000" flash; 90 lumens/second at 4 feet) at a distance of 8 feet corresponding to an exposure of 22.5 lumens/second. The resulting latent image was photodeveloped by exposure for two minutes to low-intensity light of 250 foot-candles. The lamps used for photodevelopment were two General Electric 15 watt cool-white 18 inch fluorescent lamps which were held in a conventional desk lamp. It was observed that the emulsions in which the silver halide grains had been formed in the presence of the thioether compound produced emulsions with significantly better direct-print characteristics than the emulsion in which the silver halide grains were formed in the absence of the thioether compound. For example, the coating sample of Emulsion B reached maximum density four times faster upon photodevelopment than the coating sample of Emulsion A. The exposed and photodeveloped coatings were then held for several hours under fluorescent roomlight illumination of about 600 foot-candles to ascertain their stability. At the end of this period it was evident that the coatings of the emulsions prepared with the thioether compound still exhibited good discrimination between the image and nonimage areas whereas the coating of Emulsion A, which were not prepared with the thioether compound, exhibited virtually no discrimination between the image and nonimage areas.

Example 2

An emulsion was prepared as described in Example 1, except that 2.0 grams of the thioether 1,8-dihydroxy-3,6-dithiaoctane,



per mole of silver were added to the alkali metal halide solution before the addition of the silver and lead nitrate solution. This emulsion was coated, exposed and photodeveloped as described in Example 1. The coatings of this emulsion exhibited improved direct-print properties similar to those exhibited by the use of 1,10-dithia-4,7,13,16-tetraoxycyclooctadecane as described in Example 1. Two additional coating samples of this emulsion were exposed as described above. One sample was photodeveloped as described in Example 1. The density differential between the image and nonimage areas was approximately 0.19. The second sample was photodeveloped in a similar manner except that the back of the paper base was contacted to a metal bar, heated to

100° C., during photodevelopment. The density differential in this coating had increased to 0.41.

Example 3

Two emulsions were made. One was identical to Emulsion C of Example 1. The other emulsion was similar to Emulsion C but did not contain a lead salt. Each of these emulsions was split into two portions and coated on paper supports. One portion was coated with 2.2 grams of thiosalicylic acid, as a halogen acceptor per mole of silver, while the other portion was coated without a halogen acceptor. The coatings were exposed and photodeveloped as described in Example 1. The results are summarized below.

Lead Nitrate (g./Ag mole)	Thiosalicylic Acid (g./Ag mole)	D _{max.}	D _{min.}
0	0	.13	.09
0	2.2	.22	.15
0.85	0	.19	.09
0.85	2.2	.32	.16

Thus the emulsions of my invention can be utilized to further advantage in combination with various addenda such as conventional halogen acceptors and water-soluble lead salts.

Example 4

To demonstrate the fact that various halogen acceptors may be utilized in the emulsions of my invention, an emulsion similar to Emulsion C of Example 1 was prepared and split into eight portions. To each of these portions was added the following halogen acceptors, after which they were coated on a paper support.

Halogen acceptor:	G./Ag mole
Control -----	0
Thiosalicylic acid -----	2.2
1-phenyl-3-pyrazolidone -----	40.0
Stannous chloride -----	10.0
Sodium nitrite -----	20.0
Sodium nitrite -----	40.0
Triethanolamine -----	150.0
Thiosemicarbazide -----	2.0

Samples of each of the above coatings were exposed with a high pressure mercury vapor lamp in a Honeywell Visicorder Model 906 with a galvanometer reading of 120 cycles per second and a transport speed of 25 inches per second. The samples were then photodeveloped for a few seconds to a 1000 foot-candle fluorescent light source after which a portion of each coating was covered and the remainder re-exposed to a 60 foot-candle fluorescent light source for 5 hours. All of the coatings exhibited high D_{max.}, particularly those containing the halogen acceptor.

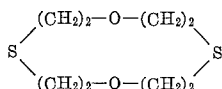
Example 5

An emulsion was prepared similar to Emulsion A in Example 1 and then split into the portions. The first portion served as a control. To the second and third portions there was added 2.0 grams of 1,10-dithia-4,7,13,16-tetraoxycyclooctadecane. The second emulsion portion was then ripened for 20 minutes at 71° C., cooled and then coated on a paper support while the third portion was held for a few minutes at 40° C. before it was coated on a paper support. Each of these coatings contained 2.2 g. of thiosalicylic acid per silver mole as a coating addendum. Samples of each of these three coatings were exposed and photodeveloped as described in Example 4. It was observed that the addition of the thioether compound as a coating addendum (i.e., after the silver halide grains were substantially in the final size and shape) at 40° C. had substantially no effect on the direct-print characteristics of this emulsion. The emulsion coatings wherein the silver halide grains were formed in the presence of the thioether compound exhibited the

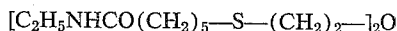
improvements described in Example 1 (Emulsions B-E) in direct-print characteristics, the second coating exhibiting the greatest improvement in $D_{\max}$ and contrast.

Example 6

Two additional emulsions were prepared in the manner utilized for Emulsion C in Example 1 except that the 1,10 - dithia-4,7,13,16-tetraoxacyclooctadecane was replaced with 4,10-dioxo-1,7-dithiacyclododecane



in one (designated Emulsion F) and with 1,17-di(N-ethyl-carbamyl)-6,12-dithia-9-oxaheptadecane



in the other (designated Emulsion G). A halogen acceptor was added to Emulsions F and G as described in Example 5 and they were coated on a paper support as described in Example 1. Samples of the coatings were then exposed and photodeveloped as described in Example 4. It was noted that both coated emulsions produced substantial increases in $D_{\max}$ when compared to comparable coated emulsion prepared in the absence of an organic thioether silver halide solvent. In addition, Emulsion G appeared to offer particularly good differentiation between the image and nonimage areas.

Example 7

This example illustrates additional types of organic thioether silver halide solvents that can be used in preparing the emulsions of the invention and that little or no sensitization is obtained from the use of such thioethers. The primary advantages obtained in a direct-print system from forming or ripening the silver halide grains in the presence of such thioethers, are a reduction in $D_{\min}$ and an increase in photodevelopment rate. The emulsion used in this example was a gelatino silver chlorobromide gelatin emulsion containing 4.7 mole percent chloride, 95 mole percent bromide, and 0.3 mole percent iodide. It was prepared as described in Example 1, Emulsion A. The emulsion was divided into several portions and treated as follows. The amounts indicated refer to grams per mole of silver halide.

(H) Control—No further treatment.

(I) 2 grams of 1,10-dithia - 4,7,13,16 - tetraoxacyclooctadecane were added to the emulsion, and it was ripened for 20 minutes at 71° C. as described in Example 5.

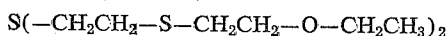
(J) The same as (I) except 4 grams of the thioether compound were used.

(K) 4 grams of the thioether compound of (I) were added to the emulsion at 40° C. just prior to coating.

(L) 5 grams of 1,8-dihydroxy - 3,6 - dithiaoctane were added to the emulsion, and it was ripened for 20 minutes at 71° C.

(M) The same as (L) except 10 grams of the thioether compound were used.

(N) The same as (I) except 2.5 grams of 3,15-dioxo-6,9,12-trithia heptadecane,

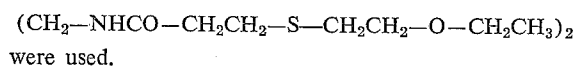


were used.

(O) The same as (N) except 5 grams of the thioether compound were used.

(P) The same as (N) except 10 grams of the thioether compound were used.

(Q) The same as (I) except 2½ grams of 10,13-diaza-3,20-dioxo-9,14-dioxo-6,17-dithiadocosane,



were used.

(R) The same as (Q) except 5 grams of the thioether compound were used.

Each of the above emulsions was coated on a paper

support. A sample of each coating was exposed through a step-wedge for 10⁻⁴ seconds in an EG and G Mark VI Sensitometer and then photodeveloped by flashing to 2,000 foot-candles for 30 minutes with white light with the following results in terms of the number of visible 0.15 log E steps obtained on exposure and photodevelopment and $D_{\min}$.

Emulsion Type	No. of Steps	60,000 F.C.M.* Photodevelopment ($D_{\min}$)
H.....	15	.29
I.....	14	.24
J.....	13	.24
K.....	14	.29
L.....	14	.24
M.....	14	.21
N.....	16	.26
O.....	15	.25
P.....	15	.25
Q.....	13	.25
R.....	15	.26

* Foot-candle-minutes.

Example 8

In order to further illustrate that the improvement in $D_{\min}$ obtained from forming or ripening the silver halide grains in the presence of certain organic thioether silver halide solvents is due to the presence of the thioether and not solely to the grain size of the silver halide crystals per se, the following comparisons were made with emulsions having the same grain sizes:

(T) A gelatino silver chlorobromide emulsions (95 mole percent bromide and 5 mole percent chloride) having an average grain size of approximately 1.5 microns was prepared by the general procedure described in Example 1 except that no iodide was used and 34 grams of sodium thiocyanate per mole of silver was added to the alkali metal halide gelatin solution as a silver halide solvent in place of the thioether compound.

(U) An emulsion was prepared similar to (T) except that in lieu of the sodium thiocyanate, 2 grams per mole of the thioether, 1,10-dithia - 4,7,13,16 - tetraoxacyclooctadecane, per mole of silver halide was added just prior to coating.

(V) An emulsion was prepared similar to (U) except that the thioether was added to the emulsion during its grain formation as described in Example 1, Emulsion C. The respective emulsions were coated on paper supports at a silver coverage of 256 mg./ft.² and a gelatin coverage of 550 mg./ft.². A sample of each coating was exposed for 60,000 foot-candle minutes with cool white fluorescent light and the $D_{\min}$'s of the respective coatings compared with the following results:

Feature addenda:	$D_{\min}$
(T) Sodium thiocyanate (added during grain formation)	.47
(U) Thioether (added just prior to coating) ---	.49
(V) Thioether (added during grain formation) -	.18

It can be seen from the above results that maximum reduction in $D_{\min}$ or background density is obtained when the silver halide grains are formed in the presence of a thioether compound, the addition of the thioether compound to the emulsion as a coating addendum not being effective, and the addition of a well-known silver halide solvent not being effective.

Example 9

A series of light-developable, direct-print, radiation-sensitive gelatino silver chlorobromide emulsions (95 mole percent bromide, 5 mole percent chloride) having silver halide grains of high internal sensitivity was prepared by utilizing various organic thioether silver halide solvents during the ripening of the silver halide emulsion. An aqueous silver nitrate solution containing 1.0 gram of lead nitrate per mole of silver nitrate was slow-

ly added to an agitated aqueous solution of gelatin, potassium bromide, sodium chloride, and a thioether silver halide solvent at 71° C. at a pH of 2.0 (adjusted with nitric acid). A control emulsion was also prepared wherein the thioether silver halide solvent was omitted. Also, for purposes of comparison, ethylene dithiocyanate was used in preparing one emulsion in lieu of a thioether of the invention. The emulsions had an average grain size of about 1.5 microns. The emulsions also contained 8.25 g. per mole of silver halide of the halogen acceptor, 1-n-butyl-1,2,5,6-tetrahydro-1,3,5-triazine-4-thio, which was added just prior to coating. The emulsions were coated on paper supports, exposed to a high intensity flash, and thereafter photodeveloped as described in Example 1 except that the photodevelopment was for five minutes to 60 foot-candles. The results are summarized in the table below.

Feature Addenda (g./Ag mole)	D _{max.}	D _{min.}	Differentiation (D _{max.} - D _{min.})
None—Control	58	44	14
2,2'-thiodiethanol, HO-(CH ₂) ₂ -S-(CH ₂) ₂ -OH (35.0 g.)	68	18	50
6,9-dioxa-3,12-dithia-tetradecane-1,14-diol, HO-(CH ₂) ₂ -S-(CH ₂) ₂ -O-(CH ₂) ₂ -S-(CH ₂) ₂ -OH (1.5 g.)	67	21	46
1,8-dihydroxy-3,6-dithiaoctane, HO-(CH ₂) ₂ -S-(CH ₂) ₂ -S-(CH ₂) ₂ -OH (2.25 g.)	67	16	51
3,6,9-trithiaundecane-1,11-diol, HO-(CH ₂) ₂ -S-(CH ₂) ₂ -S-(CH ₂) ₂ -S-(CH ₂) ₂ -OH (2.0 g.)	61	19	42
Ethylene dithiocyanate (10.0 g.)	67	51	16

Example 10

A light-developable, direct-print, radiation-sensitive gelatino silver chlorobromide photographic emulsion (95 mole percent bromide, 5 mole percent chloride) having silver halide grains of high internal sensitivity was prepared by slowly adding simultaneously an aqueous solution of silver nitrate and an aqueous solution of potassium bromide and sodium chloride to an agitated aqueous gelatin solution at 60° C. The emulsion was washed with water to remove water-soluble salts. This emulsion served as a control. Three additional emulsions were prepared in a similar manner but differed in that one contained 0.85 gram per mole of silver nitrate of lead nitrate in the silver nitrate solution, the second contained 8.0 grams per mole of silver nitrate of the thioether, 1,8-dihydroxy-3,6-dithiaoctane, in the aqueous gelatin solution, and the third contained both 0.85 gram per mole of silver nitrate of lead nitrate in the silver nitrate solution and 8.0 grams per mole of silver nitrate of 1,8-dihydroxy-3,6-dithiaoctane in the aqueous gelatin solution. Each of these emulsions was split into two parts. One part was coated with no further addendum. To the second part was added 2.2 grams per mole of silver nitrate of the halogen acceptor, thiosalicylic acid, as a coating addendum. All of the emulsions were coated on paper supports. The coatings were exposed to a Heiland-Strobnar-1 electronic flash unit (1/2000" flash, 90 lumens/second at 4 feet) at four feet and photodeveloped for 5 minutes to low-intensity light (cool white fluorescent lamps) of 250 foot-candles. One-third of each of the coatings was covered and the unmasked portion was given an additional low-intensity exposure of 50 foot-candles for one hour (3,000 FCM¹). Another one-third of each of the coatings was covered and the unmasked portion was given an additional low-intensity exposure of 50 foot-candles for an additional three hours (totaling 1200 additional FCM¹ for this portion of the coatings). The reflection densities after each exposure were read through a Wratten #15 filter with a reading on the uncoated paper support calibrated to zero. The results are summarized below.

¹ Foot-candle-minutes.

Feature Addenda	250 FCM* Photo-development	3,000 FCM* Fading	12,000 FCM* Fading
5 Control:			
D _{max.} -----	0.02	0.02	0.04
D _{min.} -----	0.02	0.02	0.04
ΔD-----	0.00	0.00	0.00
Control + halogen acceptor:			
D _{max.} -----	0.40	0.71	0.79
D _{min.} -----	0.62	0.76	0.82
ΔD-----	0.12	0.05	0.03
10 Control + lead:			
D _{max.} -----	0.02	0.04	0.07
D _{min.} -----	0.02	0.04	0.06
ΔD-----	0.00	0.00	0.01
Control + lead + halogen acceptor:			
D _{max.} -----	0.42	0.67	0.75
D _{min.} -----	0.50	0.72	0.78
ΔD-----	0.08	0.05	0.03
Control + thioether:			
D _{max.} -----	0.10	0.21	0.26
D _{min.} -----	0.08	0.14	0.18
ΔD-----	0.02	0.07	0.08
20 Control + thioether + halogen acceptor:			
D _{max.} -----	0.40	0.40	0.38
D _{min.} -----	0.26	0.26	0.27
ΔD-----	0.14	0.14	0.11
Control + lead + thioether:			
D _{max.} -----	0.22	0.29	0.30
D _{min.} -----	0.10	0.14	0.18
ΔD-----	0.12	0.15	0.12
Control + lead + thioether + halogen acceptor:			
D _{max.} -----	0.50	0.44	0.48
D _{min.} -----	0.14	0.16	0.16
ΔD-----	0.36	0.28	0.24

*Foot-candle-minutes.

The invention thus provides a new and useful class of light-developable, direct-print photographic silver halide emulsions.

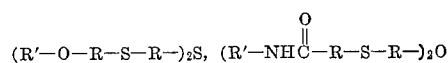
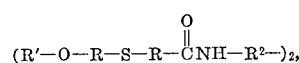
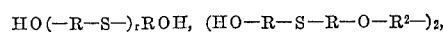
The invention has been described in considerable detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

I claim:

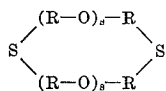
1. A light-developable, direct-print silver halide emulsion containing silver halide grains formed in the presence of an organic thioether silver halide solvent, an aqueous solution of said thioether at a 0.02 molar concentration being capable of dissolving more than twice the amount of silver chloride than that which can be dissolved by water at 60° C.

2. A light-developable, direct-print silver halide emulsion containing silver halide grains formed in the presence of an organic thioether silver halide solvent containing at least one moiety wherein ether oxygen and sulfur atoms are separated by an ethylene radical, an aqueous solution of said thioether at a 0.02 molar concentration being capable of dissolving more than twice the amount of silver chloride than that which can be dissolved by water at 60° C.

3. A light-developable, direct-print silver halide emulsion containing silver halide grains formed in the presence of an organic thioether silver halide solvent, an aqueous solution of said thioether at a 0.02 molar concentration being capable of dissolving more than twice the amount of silver chloride than that which can be dissolved by water at 60° C., and said thioether having a formula selected from the group consisting of

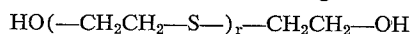


and



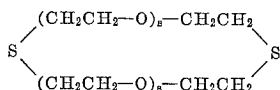
wherein R is an alkylene radical having 1 to 5 carbon atoms, R' is an alkyl radical having 1 to 5 carbon atoms, R² is an alkylene radical having 1 to 5 carbon atoms, r is an integer of 1 to 3 and s is an integer of 1 to 2.

4. A light-developable, direct-print silver halide emulsion containing silver halide grains formed in the presence of an organic thioether silver halide solvent, an aqueous solution of said thioether at a 0.02 molar concentration being capable of dissolving more than twice the amount of silver chloride than that which can be dissolved by water at 60° C., and said thioether having the formula



wherein r is an integer of 1 to 3.

5. A light-developable, direct-print silver halide emulsion containing silver halide grains formed in the presence of an organic thioether silver halide solvent, an aqueous solution of said thioether at a 0.02 molar concentration being capable of dissolving more than twice the amount of silver chloride than that which can be dissolved by water at 60° C., and said thioether having the formula



wherein s is an integer of 1 to 2.

6. A light-developable, direct-print silver halide emulsion containing silver halide grains formed in the presence of 1,17-di(N-ethylcarbamy)-6,12-dithia-9-oxaheptadecane.

7. A light-developable, direct-print silver halide emulsion containing silver halide grains formed in the presence of 3,15-dioxa-6,9,12-trithiaheptadecane.

8. A light-developable, direct-print silver halide emulsion containing silver halide grains formed in the presence of 10,13-diaza-3,20-dioxa-9,14-dioxo-6,17-dithiadocosane.

9. A light-developable, direct-print silver halide emulsion containing silver halide grains formed in the presence of 6,9-dioxa-3,12-dithiatetradecane-1,14-diol.

10. A light-developable, direct-print gelatino silver halide emulsion wherein said halide contains at least about 50 mole percent bromide and wherein the silver halide grains are formed in the presence of about 0.1 to 5 mole percent of a water-soluble lead salt based on the silver halide and about .1 to 50 grams of 2,2'-thiodiethanol per mole of silver halide.

11. A light-developable, direct-print gelatino silver halide emulsion wherein said halide contains at least about 50 mole percent bromide and wherein the silver halide grains are formed in the presence of about .01 to 5 mole percent of a water-soluble lead salt based on the silver halide and about .1 to 50 grams of 1,8-dihydroxy-3,6-dithiaoctane per mole of silver halide.

12. A light-developable, direct-print gelatino silver halide emulsion wherein said halide contains at least about 50 mole percent bromide and wherein the silver halide grains are formed in the presence of about .01 to 5 mole percent of a water-soluble lead based on the silver halide and about .1 to 50 grams of 1,17-di(N-ethylcarbamy)-6,12-dithia-9-oxaheptadecane per mole of silver halide.

13. A light-developable, direct-print gelatino silver halide emulsion wherein said halide contains at least about

50 mole percent bromide and wherein the silver halide grains are formed in the presence of about .01 to 5 mole percent of a water-soluble lead salt based on the silver halide and about .1 to 50 grams of 1,10-dithia-4,7,13,16-tetraoxacyclooctadecane per mole of silver halide.

14. A light-developable, direct-print gelatino silver halide emulsion wherein said halide contains more than about 50 mole percent bromide and wherein the silver halide grains are formed in the presence of about 0.1 to 5 mole percent of a water-soluble lead salt based on the silver halide and about .1 to 50 grams of 3,15-dioxa-6,9,12-trithiaheptadecane per mole of silver halide.

15. A light-developable, direct-print gelatino silver halide emulsion wherein said halide contains at least about 50 mole percent bromide and wherein the silver halide grains are formed in the presence of about .01 to 5 mole percent of a water-soluble lead salt based on the silver halide and about .1 to 50 grams of 10,13-diaza-3,20-dioxa-9,14-dioxo-6,17-dithiadocosane per mole of silver halide.

16. A light-developable, direct-print gelatino silver halide emulsion wherein said halide contains at least about 50 mole percent bromide and wherein the silver halide grains are formed in the presence of about .01 to 5 mole percent of a water-soluble lead salt based on the silver halide and about .1 to 50 grams of 6,9-dioxa-3,12-dithiatetradecane-1,14-diol per mole of silver halide.

17. A light-developable, direct-print gelatino silver halide emulsion wherein said halide contains at least about 50 mole percent bromide and wherein the silver halide grains are formed in the presence of about .01 to 5 mole percent of a water-soluble lead salt based on the silver halide and about .1 to 50 grams of 3,6,9-trithiaundecane-1,11-diol per mole of silver halide.

18. A light-developable, direct-print gelatino silver halide emulsion wherein said halide contains at least about 50 mole percent bromide and wherein the silver halide grains are formed in the presence of about .01 to 5 mole percent of a water-soluble lead salt based on the silver halide and about .1 to 50 grams of 4,10-dioxa-1,7-dithia-cyclododecane per mole of silver halide.

19. In the process for preparing a light-developable, direct-print silver halide emulsion, the improvement which comprises forming the silver halide grains of said emulsion in the presence of an organic thioether silver halide solvent, an aqueous solution of said thioether at a 0.02 molar concentration being capable of dissolving more than twice the amount of silver chloride than that which can be dissolved by water at 60° C.

20. A light-developable, direct-print silver halide emulsion containing silver halide grains formed in the presence of lead ions and an organic thioether silver halide solvent, an aqueous solution of said thioether at a 0.02 molar concentration being capable of dissolving more than twice the amount of silver chloride than that which can be dissolved by water at 60° C.

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