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3,220,839

PHOTOGRAPHIC EMULSIONS CONTAINING ISOTHIIOUREA DERIVATIVES

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No Drawing. Filed Aug. 25, 1961, Ser. No. 133,769
33 Claims. (Cl. 96—61)

This invention relates to photographic compositions. Preferred embodiments of the invention concern photographic silver halide emulsions containing addenda that can serve as fog-inhibiting agents or as stabilizing agents obviating the necessity of conventional fixing.

It is well known that photographic silver halide emulsions on storage tend to lose sensitivity and to become spontaneously developable without exposure to light. There is normally a detectable amount of the silver salt reduced during development in the areas where no exposure was given, this being commonly called "fog" and sometimes "chemical fog" where it is necessary to distinguish between it and the effects of accidental exposure to radiation. Fog tends to increase on storage for extended periods of time, particularly under elevated temperatures and humidities such as prevail during the summer months and in the tropics. It is thus desirable to have a method for minimizing such fog formation.

After a photographic silver halide emulsion is developed and a silver image is produced in the areas of exposure, the silver halide in the unexposed areas is conventionally washed out as a soluble complex with a fixing solution. It would be convenient to have the fixing agent incorporated directly in the emulsion. However, usual fixing agents are not suitable for incorporation directly in emulsions as they form complexes with silver halide regardless of the acidity of the environment. Also many fixing agents would cause substantial desensitization of the emulsion if incorporated therein. It is thus desirable to have fixing materials that are sufficiently compatible with photographic silver halide emulsions so that they can be utilized therein.

It is an object of this invention to provide a new class of photographic emulsion addenda.

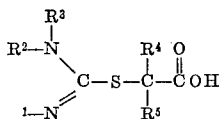
It is another object of this invention to provide novel photographic silver emulsions inhibited against fog formation.

It is another object of this invention to provide novel photographic silver halide emulsions that can be processed without the use of a conventional fixing step.

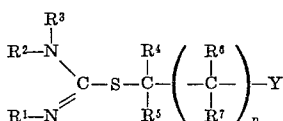
It is another object of the invention to provide novel photographic silver halide emulsions that can be developed and fixed by immersing in an aqueous alkaline solution.

It is likewise an object of this invention to provide novel photographic silver halide emulsions useful in color photography.

These and other objects of the invention are accomplished with photographic silver halide emulsions having incorporated therein isothiourea derivatives having the formulas



and



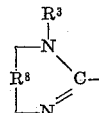
R¹, R², R³, R⁴, R⁵, R⁶ and R⁷ can be hydrogen atoms, hydrocarbon radicals such as aryl radicals as illustrated by

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phenyl radicals, alkyl-substituted phenyl and alkyl radicals and substituted alkyl radicals. R¹ and R² can also be acyl radicals having the formula



wherein R is an alkyl radical. R¹ and R² together can also be the necessary carbon and hydrogen atoms to form an alkylene radical linking both adjacent nitrogen atoms to form a cyclic nucleus as illustrated by the following moiety wherein R³ is an alkylene radical,



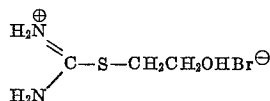
wherein R³ can be an acyl radical in addition to those substituents described above for R³. The letter n can be an integer of at least 1, and generally 1 to 10, and preferably 1 to 3. The letter Y can be a carboxyl radical, a sulfonate radical, a hydroxyl radical or an amino radical, including substituted amino radicals, of the formula



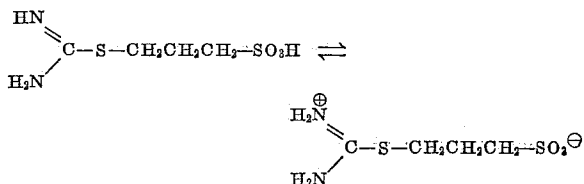
wherein R⁹ is a hydrogen atom or an alkyl radical, and wherein R¹⁰ is a hydrogen atom, an alkyl radical or an acyl radical, their salts having the formula



or a morpholino radical, Y being other than a carboxyl radical when n is 1 and R⁶ and R⁷ are hydrogen. Typical alkyl and alkylene radicals referred to above have 1 to 20 carbon atoms and more generally 1 to 4 carbon atoms. Illustrative alkyl radicals include methyl, ethyl, isopropyl, n-butyl, 2-ethylhexyl, n-decyl, stearyl, n-eicosyl and the like radicals. Alkylene radicals analogous to such alkyl radicals are suitable R⁸ substituents. The subject isothiourea derivatives are bases but can be utilized as the salts of such acids as p-toluene sulfonic acid, nitric acid, perchloric acid, hydrochloric acid, hydrobromic acid, etc. as illustrated by the salt,



The isothiourea derivatives of the invention also exist as inner salts as illustrated by the following equation,



German Patent 1,031,303, published June 4, 1958, describes the preparation of typical isothiourea derivatives of the invention.

The isothiourea derivatives of the invention can be utilized in photographic silver halide emulsions to reduce incubation fog. These addenda serve to stabilize emulsions under prolonged storage conditions or under conditions of high temperature and humidity which typically occur in summer months or in tropical climates. The amount of the subject addenda that is used in photographic silver halide emulsions for antifoggant purposes can be

varied in accordance with usual practice, the amount utilized varying with the effect desired, degree of ripening, silver content of the emulsion, etc. Generally from about .001 to 10 grams of the isothiourea per mole of silver halide are suitable for antifoggant purposes.

The isothiourea derivatives of the invention can also serve as incorporated fixing agents. These addenda do not prevent development of exposed areas of the emulsion but protect the unexposed areas of the emulsion against print out after development of the emulsion. Thus with emulsions containing the addenda of the invention silver images can be formed and stabilized without the use of a conventional fixing process. The subject addenda are stable and do not act as fixing agents in acidic or neutral media such as in emulsions. However, under aqueous alkaline conditions, such as often times prevail during the developing of photographic emulsions, the subject addenda become active fixing agents. If the developing solution is not sufficiently alkaline to activate the isothiourea derivatives of the invention, the photographic element having the developed emulsion coated thereon can thereafter be immersed in a stronger alkaline bath for fixing. Under such conditions a soluble complex is formed with the silver halide in the unexposed and undeveloped areas of the emulsion. When the subject addenda are used in photographic silver halide emulsions as fixing agents, at least one mole of the addenda is utilized for each mole of silver halide in the emulsion.

In addition to serving as antifoggants and as fixers in photographic silver halide emulsions, the isothiourea derivatives of the invention can also serve in some silver halide emulsions to increase sensitivity, D_{\max} , and contrast in emulsions. These improved properties are also imparted to photographic silver halide emulsions when the isothiourea addenda of the invention are incorporated into gelatin layers coated adjacent to the photographic silver halide emulsions.

The preparation of photographic silver halide emulsions such as are used with the addenda of this invention involves three separate operations: (1) emulsification and digestion of silver halide, (2) the freeing of the emulsion of excess water-soluble salts, suitably by washing with water, and (3) the second digestion or "after-ripening" to obtain increased emulsion speed or sensitivity. (Mees, "The Theory of the Photographic Process," 1954.) The addenda of the invention can be added to the emulsion before the final digestion or after-ripening, or they can be added immediately prior to the coating.

The addenda of the invention can be added to photographic emulsions using any of the well-known techniques in emulsion making. For example, they can be dissolved in a suitable solvent and added to the silver halide emulsion, or they can be added to the emulsion in the form of a dispersion similar to the technique used to incorporate certain types of color-forming compounds (couplers) in a photographic emulsion. Techniques of this type are described in Jelley et al. U.S. Patent 2,322,027, issued June 15, 1943, and Fierke et al. U.S. Patent 2,801,171, issued July 30, 1957. The solvent should be selected so that it has no harmful effect upon the emulsion in accordance with usual practice, and generally solvents or diluents which are miscible with water are to be preferred.

The emulsions of the invention can include the usual photographic emulsion addenda including chemical sensitizers, optical sensitizers, stabilizers or antifoggants, plasticizers, hardeners, coating aids, and the like.

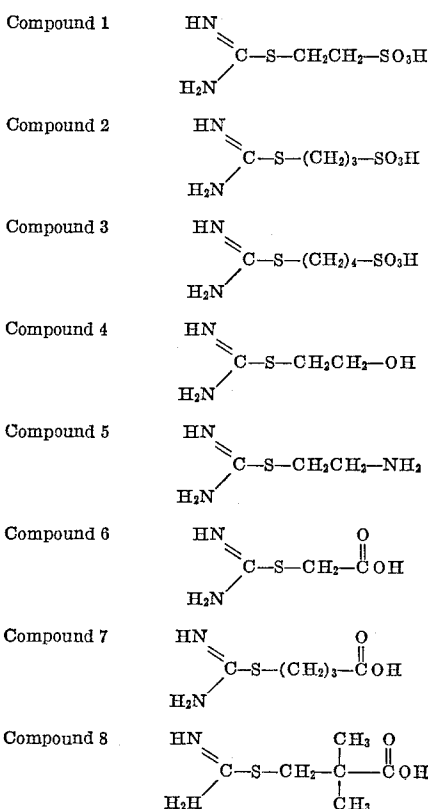
Various silver salts can be used as the sensitive salt such as silver bromide, silver iodide, silver chloride, or mixed silver halides such as silver chlorobromide or silver bromoiodide.

In the preparation of the silver halide dispersions employed for preparing silver halide emulsions, there can be employed as the dispersing agent for the silver halide in its preparation, gelatin or some other colloidal material such as colloidal albumin, a cellulose derivative, or a synthetic

resin, for instance, a polyvinyl compound, although gelatin is preferred. Some colloids which 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 30-60% and a specific viscosity of 0.25-1.5 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 cyanoacetyl 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. If desired, compatible mixtures of two or more of these colloids can be employed for dispersing the silver halide in its preparation.

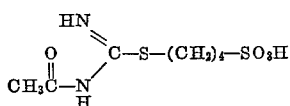
The above-described emulsions of the invention can be coated on a wide variety of supports in accordance with usual practice. Typical supports for photographic elements of the invention include cellulose nitrate film, cellulose acetate film, polyvinyl acetal film, polystyrene film, polyethyleneterephthalate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

The invention is further illustrated by the following examples of preferred embodiments thereof. Typical isothiourea derivatives of the invention are numbered and listed below, the numbers given the addenda below being used to indicate these addenda in the tables or examples hereinafter.

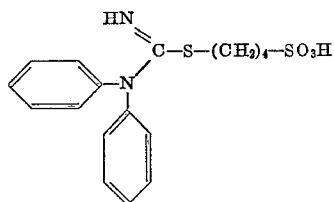


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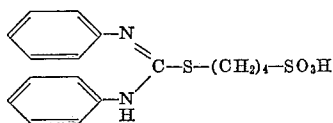
Compound 9



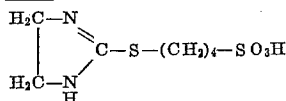
Compound 10



Compound 11



Compound 12



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usual manner. Test samples containing no isothiurea addenda of the invention were also included in the tests for purposes of comparison. The developer had the following formula:

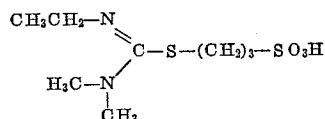
	Grams
N-methyl-p-aminophenol sulfate	2
Hydroquinone	8
Sodium sulfite (anhydrous)	90
Sodium carbonate monohydrate	52.5
Potassium bromide	5
Water to make one liter.	

The results of the sensitometric tests are summarized by the data set out in Table A below. In Table A the speeds indicated are a function of the exposure necessary to give a density of 0.3 above background fog and expressed as a reciprocal relation to exposure, the initial control speed being taken as 100 in each case. The feature addenda in Table A correspond in number to the formulas set out above. The concentrations of addenda are indicated in Table A as grams of addenda per mole of silver halide in the emulsion.

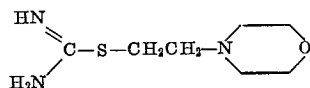
Table A

Addenda	Conc. of Addenda	Original Test			120° F., 50% R.H.			
					1 Week			2 Weeks
		Speed	γ	Fog	Speed	γ	Fog	Fog
Control	0	100	.88	.08	145	.76	.19	.50
Compound 1	2.85	94	.80	.07	126	.68	.14	.27
Do	5.7	82	.83	.07	112	.71	.10	.22
Compound 2	6.18	89	.91	.07	132	.62	.14	.30
Compound 3	6.16	83	.79	.07	145	.66	.16	.38
Control	0	100	.90	.07	-----	-----	-----	.58
Compound 1	.3	110	.85	.07	-----	-----	-----	.44
Do	3.0	100	.93	.06	-----	-----	-----	.29

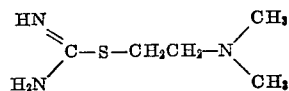
Compound 13



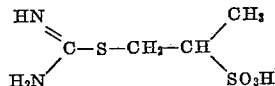
Compound 14



Compound 15



Compound 16

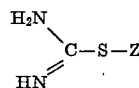


EXAMPLE 1

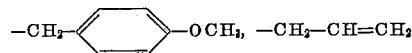
Typical isothiurea derivatives of the invention were incorporated into a high speed negative-type gelatino-silver bromiodide emulsion which was sulfur and gold sensitized. The emulsion was coated on cellulose acetate film supports at a coverage of about 355 mg. of silver and about 840 mg. of gelatin per square foot. The prepared photographic elements were then exposed, both initially and after 1 and 2 weeks' storage at 120° F. and a relative humidity of 50%, in the form of film strips in an Eastman Type Ib sensitometer, developer for 4 minutes at 68° F., and then fixed, washed and dried in the

As can be observed from the data set out in the above table, the addenda of the invention impart substantial antifoggant properties to photographic silver halide emulsions. We have found that only certain isothiurea derivatives are useful photographic addenda, it being highly unpredictable which derivative of this general class of compounds has utility. For example, if one of the compounds listed below is utilized in the emulsion of this example at a concentration of 3.0 grams per mole of silver halide, the fog level after the two week incubation period exceeds the control sample:

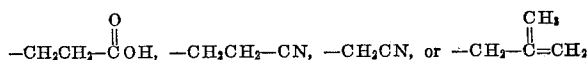
55



60 wherein Z is



65



EXAMPLE 2

Additional addenda of the invention were incorporated into a photographic high speed negative-type gelatino-silver bromiodide emulsion panchromatically sensitized with a cyanine dye and coated on a cellulose acetate film support and tested as described in Example 1 except the test samples, after exposure in the sensitometer, were

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developed for 5 minutes at 68° F. in a developer having the formula:

	Grams
N-methyl-p-aminophenol sulfate	2.5
Hydroquinone	2.5
Sodium sulfite (anhydrous)	30
Sodium borate	10
Potassium bromide	0.5
Water to make one liter.	

The results of the sensitometric tests are summarized by the data set out in Table B below wherein the speeds and concentration units are as described for the data in Table A.

Table B

Addenda	Conc. of Addenda	Original Test		120° F., 50% R.H., 1 Week	
		Speed	Fog	Speed	Fog
Control	0	100	.18	87	.38
Compound 11	0.3	95	.15	83	.26
Do	3.0	80	.12	57	.22
Compound 12	3.0	102	.14	80	.27

The data in Table B further illustrates the antifoggant properties of the subject isothiourea derivatives.

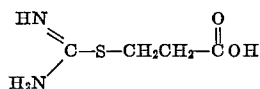
EXAMPLE 3

The determination of the antifoggant properties of several additional addenda of the invention was carried out by the general procedure described in Example 1. The emulsion was a fast negative-type gelatino-silver bromoiodide emulsion which was gold and sulfur sensitized and coated on a cellulose acetate film support as described in Example 1. The results of the tests are summarized by the data set out in Table C below.

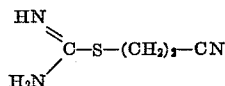
Table C

Addenda	Conc. of Addenda	Original Test		120° F., 50% R.H.		
		Speed	Fog	1 Week		2 Weeks
				Speed	Fog	
Control	0	100	.08	123	.21	.50
Compound 1	2.7	97	.07	138	.11	.26
Do	5.2	97	.07	135	.10	.22
Compound 4	0.15	87	.07	107	.12	.24
Compound 5	0.09	97	.08	135	.16	.34
Control	0	100	.11	110	.28	-----
Compound 4	0.54	97	.07	71	.14	-----
Compound 9	0.15	97	.08	110	.19	-----
Do	0.225	100	.07	126	.16	-----
Compound 10	0.33	91	.08	110	.17	-----
Control	0	100	.10	-----	.20	.54
Compound 6	2.05	105	.08	-----	.18	.40
Do	6.15	112	.08	-----	.16	.30

When the next higher homologue of Compound 6, a compound having the formula



was substituted for Compound 6 in the emulsion, a fog of greater than 1.0 resulted after the two week incubation at 120° F. and 50% relative humidity. Likewise, a high fog of .98 resulted after a similar two week incubation period when a compound having the formula



was substituted in the emulsion for the isothiourea derivatives of the invention. The ineffectiveness of these lat-

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ter addenda as antifoggants in photographic silver halide emulsions further illustrates the high degree of unpredictability in the present art.

EXAMPLE 4

A 4.0 gram portion of Compound 2 and 5.0 grams of gelatin were dissolved in 40.0 ml. of hot water. To the resulting mixture was added 4.0 ml. of a concentrated negative-type medium speed gelatino-silver bromoiodide emulsion of the type described by Trivelli and Smith in the Phot. Jour., vol. 79, pp. 330-331 (1939), and the resulting emulsion coated on a cellulose acetate film support. The resulting photographic element was then exposed to an image, developed for 2 minutes at 68° F. in the developer described in Example 2 and then immersed in 10% tetramethylammonium hydroxide for 1 minute. The unexposed image areas of the resulting film were transparent and colorless and did not darken upon prolonged exposure to light. Similar results are obtained when Compounds 1 and 3 to 16 described hereinabove are substituted for Compound 2. This example illustrates developing photographic silver halide emulsions containing isothiourea derivatives of the invention in a conventional developer and thereafter fixing the resulting developed image by immersing in a stronger aqueous alkaline solution for faster fixing action.

EXAMPLE 5

To 20.0 ml. of a 10% gelatin solution was added 20.0 ml. of a 5% solution of Compound 2. To the resulting mixture was added 0.25 gram of 1-phenyl-3-pyrazolidone and 4.0 ml. of the concentrated negative-type medium speed gelatino-silver bromoiodide emulsion referred to in Example 4. The resulting photographic emulsion was then coated on a 40-pound photographic paper support with a waterproof backing that had previously been soaked in a 5% solution of Compound 2 and partially dried on a heated coating block. The coated paper was then exposed to an image and immersed for 2 minutes in a solution containing 2.5% sodium hydroxide and 10% sodium sulfate, after which the paper was light stable without washing. This example illustrates the use of a photographic silver halide emulsion containing both an isothiourea fixer derivative of the invention and a 3-pyrazolidone developer, and the developing and fixing of this emulsion by immersing in an aqueous alkaline solution having a pH greater than 7.

EXAMPLE 6

To 20.0 ml. of a 10% gelatin solution was added 20.0 ml. of a 10% solution of Compound 2 and 0.25 gram of 1-phenyl-3-pyrazolidone. To the resulting mixture was added 3.5 ml. of the concentrated negative-type medium speed gelatino-silver bromoiodide emulsion referred to in Example 4. The resulting emulsion was then coated on a 10-pound photographic paper stock having a waterproof backing. The coated paper was then exposed to an image and immersed for 1 minute in a solution of 10% tetramethylammonium hydroxide containing 1% L-ascorbic acid. The resultant image exhibited good quality and was light stable. This example and following Examples 7 and 8 further illustrate substantially concomitant developing and fixing of photographic silver halide emulsions containing both isothiourea derivatives of the invention and a developer by immersing in an aqueous alkaline solution.

EXAMPLE 7

To 20.0 ml. of a 10% gelatin solution was added 20.0 ml. of a 15% solution of Compound 2. To the resulting solution was added 5.0 ml. of the concentrated negative-type medium speed gelatino-silver bromoiodide emulsion referred to in Example 4. To the resulting emulsion

was added 2.0 ml. of 10% 1-phenyl-3-pyrazolidone in ethanol and 4.0 ml. of a 10% aqueous solution of L-ascorbic acid. The emulsion was then coated on a cellulose acetate film support. After exposure to an image, the coated emulsion was immersed in a 10% tetramethylammonium hydroxide solution for 15 seconds whereupon the film had developed and cleared producing an image of good quality and light stability.

EXAMPLE 8

To 20.0 ml. of a 10% gelatin solution was added 20.0 ml. of a 10% solution of Compound 1. To this solution was added 0.25 gram of 1-phenyl-3-pyrazolidone and 0.5 gram of L-ascorbic acid. Then 3.5 ml. of the concentrated negative-type medium speed gelatino-silver bromoiodide emulsion referred to in Example 4 were added. The resulting emulsion was then coated on photographic paper stock. The coated emulsion was exposed to an image and immersed for 1 minute in a 10% solution of tetramethylammonium hydroxide. Thereafter the image on the photographic element was stable to light.

EXAMPLE 9

A high speed negative-type gelatino-silver bromoiodide emulsion similar to that described in Example 1 containing Compound 2 was coated on a photographic paper support at a coverage of 70 mg. of silver per square foot, 0.245 gram of Compound 2 per square foot also being present in the coated emulsion. A photographic element having two layers coated on photographic paper was also prepared wherein Compound 2 dispersed in a gelatin undercoat at a concentration of 0.195 gram per square foot having coated thereon a layer of the described gelatino-silver bromoiodide emulsion free of Compound 2. A control gelatino-silver bromoiodide emulsion free of Compound 2 was also prepared. A sample of each coating was then exposed in an Eastman Ib sensitometer, processed in an X-ray developer for 25 seconds at 32° C., and then fixed, washed and dried in the usual manner. The developer had the following formula:

	G.
Hydroquinone	8.8
N-methyl-p-aminophenol sulfate	2.2
Sodium sulfite (anhydrous)	72.0
Sodium carbonate (anhydrous)	48.0
Potassium bromide	4.0
Water to make 1 liter.	

The results of the sensitometric tests are summarized by the data set out in Table D below.

Table D

Coating	D _{max.}	Relative Speed	Bar γ (Contrast)
A. Control.....	0.68	100	0.42
B. Compound 2 in gelatino-silver bromoiodide emulsion.....	1.03	204	0.56
C. Gelatino-silver bromoiodide emulsion coated on a gelatin emulsion containing Compound 2.....	1.01	170	0.65

The data in Table D illustrates the increased speed, D_{max.} and contrast obtained especially in high temperature, rapid processing of emulsions containing the subject isothiourea derivatives. Also, this data illustrates that the subject isothiourea derivatives impart useful properties to photographic emulsion when utilized in adjacent emulsion layers.

The isothiourea derivatives of the invention can be utilized in emulsions processed in color reversal processes. Such addenda are particularly useful for increasing reversal D_{max.} that is generally decreased when thio sensitizers are utilized in the emulsion. Example 10 below illustrates such utility.

EXAMPLE 10

In a high-speed gelatino-silver bromoiodide emulsion was dispersed an open-chain coupler having a reactive methylene group suitable for forming a yellow image with oxidized color developer, e.g. coupler Nos. I to V of McCrossen et al. U.S. Patent 2,875,057 in dibutyl phthalate. Separate coatings of the yellow coupler-containing emulsion were prepared which included thio sensitizers and mixtures of the thio sensitizers and Compound 2, as well as a control sample, coated on a cellulose acetate film support. The prepared photographic elements were then exposed in an Eastman Ib sensitometer and processed in a color reversal process. The results of the test are summarized by the data set out in Table E below. In Table E, the concentrations of addenda are in grams per mole of silver halide in the emulsion.

Table E

Addenda	D _{max.}	Relative Speed
A. Control.....	3.70	100
B. 1 g. of poly(thiodiethylene succinate).....	3.00	282
C. 1 g. of poly(thiodiethylene succinate) plus 3 g. of Compound 2.....	3.36	200
D. 3 g. of 1,10-dithia-4,4,13,16-tetraoxacyclooctadecane.....	2.29	363
E. 3 g. of 1,10-dithia-4,4,13,16-tetraoxacyclooctadecane plus 3 g. of Compound 2.....	3.04	302
F. .875 g. of 14,16-diaza-4,7-dioxa-3,17-dioxo-1,10-dithia cyclononadecane.....	3.53	135
G. .875 g. of 14,16-diaza-4,7-dioxa-3,17-dioxo-1,10-dithia cyclononadecane plus 3 g. of Compound 2.....	3.70	126

The data in Table E illustrates the improvement in D_{max.} imparted by the isothiourea addenda of the invention when utilized with thio sensitizers. The color reversal process utilized is described below. The exposed film was developed in a developer having the following composition:

Sodium hexametaphosphate	g--	2.0
N-methyl-p-aminophenol sulfate	g--	6.0
Sodium sulfite, anhydrous	g--	50.0
Hydroquinone	g--	6.0
Sodium carbonate monohydrate	g--	35.0
Potassium bromide	g--	2.0
Sodium thiocyanate	g--	1.5
0.5% solution of 6-nitrobenzimidazole nitrate.....	cc--	12.0
0.1% solution of potassium iodide	cc--	10.0
Water to make 1 liter.		

The element was then thoroughly washed with water and treated in a hardening bath having the following composition:

Potassium chrome alum crystals	g--	30.0
Water to make 1 liter.		

The element was then thoroughly washed with water and treated for 30 seconds in a solution having the following composition:

	G.
Sodium borohydride	0.25
Sodium hydroxide	4.0
Water to make 1 liter.	

The element was then treated in a color developer having the following composition:

Benzyl alcohol	cc--	6.0
Sodium hexametaphosphate	g--	2.0
Sodium sulfite, anhydrous	g--	5.0
Trisodium phosphate	g--	40.0
Potassium bromide	g--	0.25
0.1% solution of potassium iodide	cc--	10.0

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Sodium hydroxide	g	6.5
Color developer *	g	11.33
Ethylenediamine sulfate	g	7.8
Citrazinic acid	g	1.5
Water to make 1 liter.		

*=4-amino-N-ethyl - N - (β - methanesulfonamidoethyl) - m-toluidine sesquisulfate monohydrate.

The element was then thoroughly washed with water and treated in a clearing and fixing bath having the following composition:

	G.
Sodium thiosulfate	150.0
Sodium bisulfite	20.0
Water to make 1 liter.	

The element was then treated in a bleach bath having the following composition:

	G.
Potassium dichromate	5.0
Potassium ferricyanide	70.0
Potassium bromide	20.0
Water to make 1 liter.	

The element was again washed and treated once again with the clearing and fixing bath identified above. The element was again washed and treated in a stabilizing bath having the following composition:

Formaldehyde (37% by weight)	cc	7.0
Dispersing agent *	g	0.5
Water to make 1 liter.		

*Such as Triton-X 100, i.e., an alkylaryl polyether alcohol (octylphenoxy polyethoxy ethanol).

EXAMPLE 11

A high speed gelatino-silver bromiodide emulsion which was optically sensitized in the region of 5000 to 6000 angstroms and containing dispersed therein a pyrazolone coupler suitable for forming a magenta image with oxidized color developer, e.g., coupler Nos. 7, etc., of Fierke et al., U.S. Patent 2,801,171 (column 2), was prepared. The prepared emulsion was divided into several portions, one portion coated on a cellulose acetate film support without further emulsion addenda, and other portions coated on the film support with a thio sensitizer and a mixture of the thio sensitizer and Compound 1. The prepared photographic elements were then exposed in an Eastman Ib sensitometer and thereafter processed in a color negative process of the general type described in "Journal of the Society of Motion Picture and Television Engineers," vol. 61 (1953), pages 667-701. The results of the test are summarized by the data set out in Table F below wherein the concentrations of addenda are in grams per mole of silver halide in the emulsion and the speed is measured at a density of 0.2 above background fog.

Table F

Addenda	Relative Fog	Relative Speed
A. Control	0	100
B. 3 g. of poly(thiodiethylene glutarate)	+ .12	204
C. 3 g. of poly(thiodiethylene glutarate) plus 1 g. of Compound 1	-.07	178

The data in Table F illustrates the antifoggant properties of the subject isothiurea derivatives in emulsions containing thio sensitizers used in color photography.

EXAMPLE 12

A high speed gelatino-silver bromiodide emulsion which was optically sensitized in the region of 6000 to 7000 angstroms and containing dispersed therein a phenolic coupler suitable for forming a cyan image with oxidized color developer, e.g., coupler Nos. 1 to 6 of Fierke et al. U.S. Patent 2,801,171 (column 2) in a solvent such as tri-o-cresylphosphate, was prepared. The

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prepared emulsion was divided into several portions, one portion coated on a cellulose acetate film support without further emulsion addenda, and other portions coated on the film support with varying amounts of Compound 2 described above. The prepared photographic elements were then exposed, initially and also after one week of incubation at 120° F. and 50% relative humidity, in an Eastman Ib sensitometer and thereafter processed in a color negative process of the general type described in "Journal of the Society of Motion Picture and Television Engineers," vol. 61 (1953), pages 667-701. The results of the test are summarized by the data set out in Table G below wherein the concentrations of addenda are in grams per mole of silver halide in the emulsion and the speed is measured at a density of 0.2 above background fog.

Table G

Addenda	Conc. of Addenda	Original Test		1 Week at 120° F., 50% R.H.	
		Speed	Fog	Speed	Fog
Control	0	100	.46	83	.62
Compound 2	1	105	.20	110	.22
Do.	2	102	.18	107	.21

The data in Table G further illustrates the antifoggant properties of the subject thiourea derivatives.

EXAMPLE 13

Additional addenda of the invention were incorporated into a photographic high speed negative-type gelatino-silver bromiodide emulsion panchromatically sensitized with a cyanine dye and coated on a cellulose acetate film support and tested as described in Example 2. The results of the sensitometric tests are summarized by the data set out in Table H below wherein the speeds and concentration units are as described by the data in Table A.

Table H

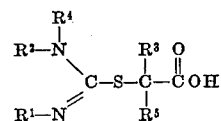
Addenda	Conc. of Addenda	Original Test		2 Weeks at 120° F., 50% R.H.
		Speed	Fog	
Control	0	100	.13	.59
Compound 7	1.5	82	.11	.22
Do.	3.0	100	.11	.13
Control	0	100	.12	.70
Compound 8	.3	80	.11	.33
Do.	1.5	73	.10	.12

The hydrobromide salt of Compound 7 was utilized in this example.

Although the invention has been described in detail with reference to certain preferred embodiments thereof, 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.

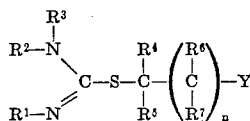
We claim:

1. A photographic silver halide emulsion containing at least one mole per mole of silver halide of an isothiurea derivative having a formula selected from the group consisting of



13

and



wherein:

- (1) R^3 , R^4 , R^5 , R^6 and R^7 are selected from the group consisting of
 - (a) hydrogen,
 - (b) alkyl, and
 - (c) phenyl;
- (2) R^1 and R^2 are selected from the group consisting of
 - (a) hydrogen,
 - (b) alkyl,
 - (c) phenyl,
 - (d) acyl having the formula



wherein R is alkyl, and

- (e) the necessary carbon and hydrogen atoms which together form alkylene linking both adjacent nitrogen atoms to form a heterocyclic nucleus;
- (3) n is an integer of 1 to 10; and
- (4) Y is selected from the group consisting of
 - (a) amino,
 - (b) carboxyl,
 - (c) sulfonyl, and
 - (d) hydroxyl;

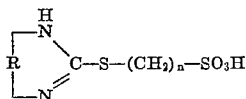
Y being other than carboxyl when n is 1 and R^6 and R^7 are hydrogen atoms.

2. A photographic silver halide emulsion as described in claim 1 wherein the isothiourea derivative is in water-soluble salt form.

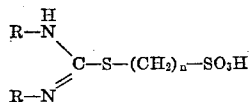
3. A photographic emulsion support having coated thereon a photographic silver halide emulsion as described in claim 1.

4. The process for fixing an exposed and developed photographic element as described in claim 3 which comprises treating said element in an aqueous alkaline medium and thereby forming a complex with the isothiourea derivative and unexposed and undeveloped silver halide of said element.

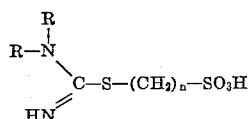
5. A photographic silver halide emulsion containing at least one mole per mole of silver halide of an isothiourea derivative having the formula

wherein n is an integer of 2 to 4 and R is alkylene.

6. A photographic silver halide emulsion containing at least one mole per mole of silver halide of an isothiourea derivative having the formula

wherein n is an integer of 2 to 4 and R is phenyl.

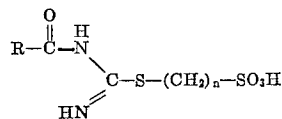
7. A photographic silver halide emulsion containing at least one mole per mole of silver halide of an isothiourea derivative having the formula

wherein n is an integer of 2 to 4 and R is phenyl.

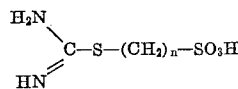
8. A photographic silver halide emulsion containing

14

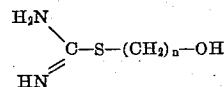
at least one mole per mole of silver halide of an isothiourea derivative having the formula

wherein n is an integer of 2 to 4 and R is alkyl.

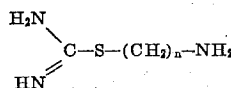
9. A photographic silver halide emulsion containing at least one mole per mole of silver halide of an isothiourea derivative having the formula

wherein n is an integer of 2 to 4.

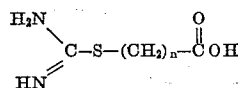
10. A photographic silver halide emulsion containing at least one mole per mole of silver halide of an isothiourea derivative having the formula

wherein n is an integer of 2 to 4.

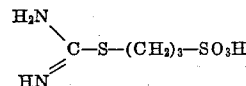
11. A photographic silver halide emulsion containing at least one mole per mole of silver halide of an isothiourea derivative having the formula

wherein n is an integer of 2 to 4.

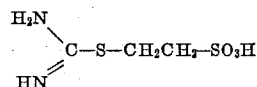
12. A photographic silver halide emulsion containing at least one mole per mole of silver halide of an isothiourea derivative having the formula

wherein n is an integer selected from the group consisting of 1, 3 and 4.

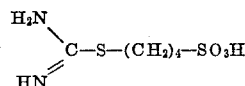
13. A photographic gelatino-silver halide emulsion containing at least one mole per mole of silver halide of an isothiourea derivative having the formula



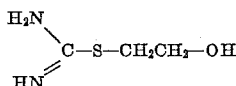
14. A photographic gelatino-silver halide emulsion containing at least one mole per mole of silver halide of an isothiourea derivative having the formula



15. A photographic gelatino-silver halide emulsion containing at least one mole per mole of silver halide of an isothiourea derivative having the formula



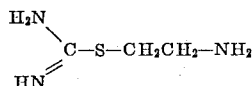
16. A photographic gelatino-silver halide emulsion containing at least one mole per mole of silver halide of an isothiourea derivative having the formula



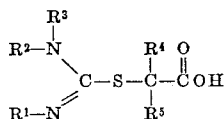
17. A photographic gelatino-silver halide emulsion con-

15

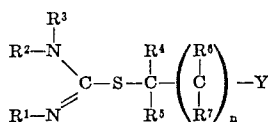
taining at least one mole per mole of silver halide of an isothiourea derivative having the formula



18. A photographic silver halide emulsion containing at least about .001 gram per mole of silver halide of an isothiourea derivative having a formula selected from the group consisting of



and



wherein:

- (1) R^3 , R^4 , R^5 , R^6 and R^7 are selected from the group consisting of
 - (a) hydrogen,
 - (b) alkyl, and
 - (c) phenyl;
- (2) R^1 and R^2 are selected from the group consisting of
 - (a) hydrogen,
 - (b) alkyl,
 - (c) phenyl, and
 - (d) acyl having the formula



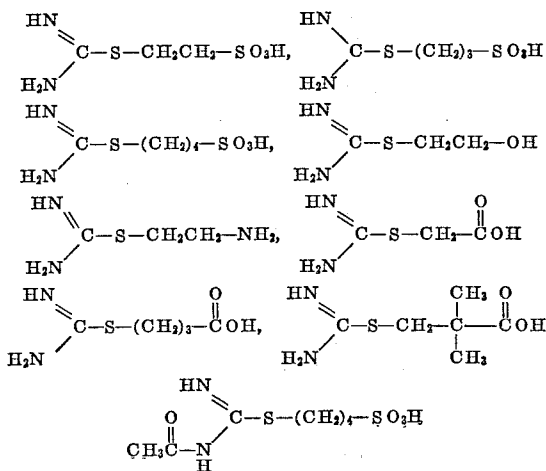
wherein R is alkyl;

- (3) n is an integer of 1 to 10; and
- (4) Y is selected from the group consisting of
 - (a) amino,
 - (b) carboxyl,
 - (c) sulfonyl, and
 - (d) hydroxyl;

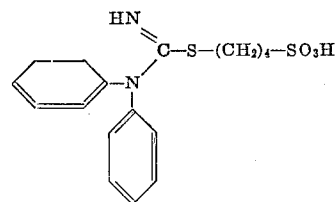
Y being other than carboxyl when n is 1 and R^6 and R^7 are hydrogen atoms.

19. A photographic silver halide emulsion as described in claim 18 which contains a coupler compound selected from the class consisting of phenolic, pyrazolone and open-chain reactive methylene compounds capable of forming a dye with the oxidation product of an aromatic primary amine silver halide color developing agent.

20. A photographic silver halide emulsion containing at least about .001 gram per mole of silver halide of an isothiourea derivative having a formula selected from the group consisting of

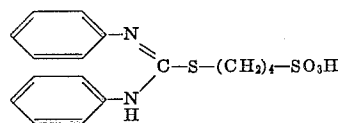


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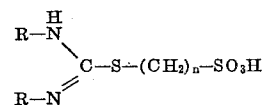
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10 and



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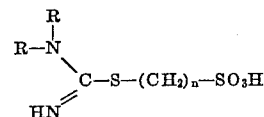
21. A photographic silver halide emulsion containing about .001 to 10 grams per mole of silver halide of an isothiourea derivative having the formula



20

wherein n is an integer of 2 to 4 and R is phenyl.

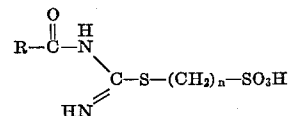
22. A photographic silver halide emulsion containing about .001 to 10 grams per mole of silver halide of an isothiourea derivative having the formula



30

wherein n is an integer of 2 to 4 and R is phenyl.

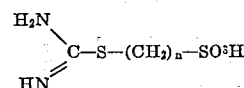
23. A photographic silver halide emulsion containing about .001 to 10 grams per mole of silver halide of an isothiourea derivative having the formula



40

wherein n is an integer of 2 to 4 and R is alkyl.

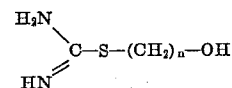
24. A photographic silver halide emulsion containing about .001 to 10 grams per mole of silver halide of an isothiourea derivative having the formula



50

wherein n is an integer of 2 to 4.

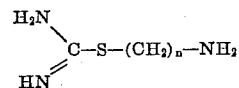
25. A photographic silver halide emulsion containing about .001 to 10 grams per mole of silver halide of an isothiourea derivative having the formula



55

wherein n is an integer of 2 to 4.

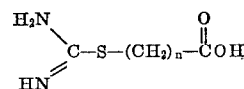
26. A photographic silver halide emulsion containing about .001 to 10 grams per mole of silver halide of an isothiourea derivative having the formula



65

wherein n is an integer of 2 to 4.

27. A photographic silver halide emulsion containing about .001 to 10 grams per mole of silver halide of an isothiourea derivative having the formula

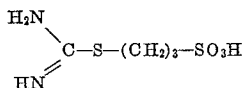


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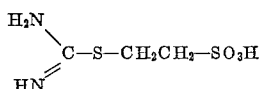
17

wherein n is an integer selected from the group consisting of 1, 3 and 4.

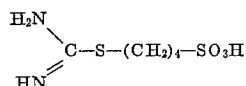
28. A photographic silver halide emulsion containing about .001 to 10 grams per mole of silver halide of an isothiurea derivative having the formula



29. A photographic silver halide emulsion containing about .001 to 10 grams per mole of silver halide of an isothiurea derivative having the formula



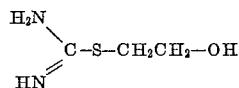
30. A photographic silver halide emulsion containing about .001 to 10 grams per mole of silver halide of an isothiurea derivative having the formula



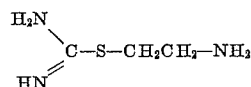
31. A photographic silver halide emulsion containing

18

about .001 to 10 grams per mole of silver halide of an isothiurea derivative having the formula



32. A photographic silver halide emulsion containing about .001 to 10 grams per mole of silver halide of an isothiurea derivative having the formula



33. A photographic emulsion support selected from the group consisting of cellulose acetate film, polystyrene film, polyethyleneterephthalate film and paper having coated thereon a photographic silver halide emulsion as described in claim 18.

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2,819,965	1/1958	Murray	96-109
2,899,306	8/1959	Spath	96-66 X

NORMAN G. TORCHIN, *Primary Examiner*.

HAROLD N. BURSTEIN, *Examiner*.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

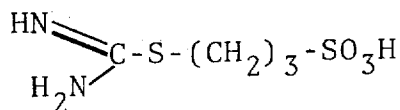
Patent No. 3,220,839

November 30, 1965

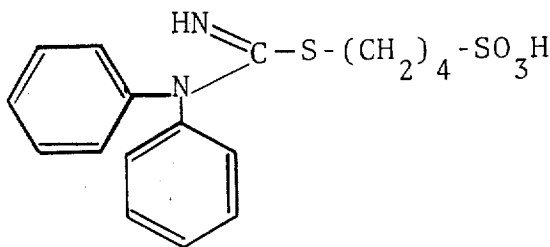
Arthur H. Herz et al.

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

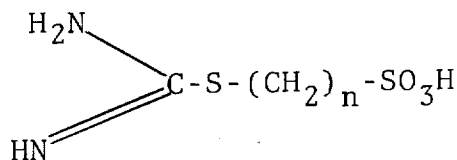
Column 15, lines 56 to 60, first formula at the right should appear as shown below instead of as in the patent:



column 16, lines 1 to 8, the formula should appear as shown below instead of as in the patent:



same column 16, lines 47 to 50, the formula should appear as shown below instead of as in the patent:



Signed and sealed this 18th day of October 1966.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents