United States Patent

[11] 3,615,618

[72] Inventors **Albert W. Wise; John W. Gates, Jr.; Dorothy J. Beavers, all of Rochester, N.Y.**

[21] Appl. No. **816,867**
[22] Filed **Apr. 4, 1969**
[45] Patented **Oct. 26, 1971**

[73] Assignee **Eastman Kodak Company Rochester, N.Y.**

[54] PHOTOGRAPHIC SILVER HALIDE COMPOSITIONS COMPRISING THIOURAZOLE ADDUCTS

19 Claims, No Drawings

[52] **U.S. Cl.** **96/109,** 96/66.5, 96/107
[51] **Int. Cl.** **G03c 1/28,** G03c 1/34, G03c 5/30
[50] **Field of Search** 96/107, 108, 109, 66.5

[56] **References Cited**

UNITED STATES PATENTS

3,148,987	9/1964	Williams	96/107
3,433,640	3/1969	Nishio et al.	96/107
3,447,927	6/1969	Bacon et al.	96/107

Primary Examiner—Norman G. Torchin
Assistant Examiner—Richard E. Fichter
Attorneys—W. H. J. Kline, B. D. Wiese and Gerald E. Battist

ABSTRACT: This invention relates to photographic compositions comprising adducts of thiourazoles, including dithiourazoles, with $\alpha\beta$-unsaturated compounds. Typical useful adducts are made with $\alpha\beta$-unsaturated acids, aldehydes, amides, ketones and esters and include monoadducts and diadducts of the thiourazoles.

PHOTOGRAPHIC SILVER HALIDE COMPOSITIONS COMPRISING THIOURAZOLE ADDUCTS

This invention relates to new photographic compositions. In one aspect, this invention relates to photographic compositions comprising an adduct of an α, β-unsaturated compound with a thiourazole. In another aspect, this invention relates to new silver halide photographic compositions having reduced minimum density in image areas upon development and after aging and development. In still another aspect, this invention relates to heat-stabilized printout silver halide emulsions having reduced minimum density and better stability.

It is known in the art that urazole compounds and dithiourazole compounds such as 1-phenyl-3,5-dithiourazole are known in the art as antiplumming agents and/or antifogging agents. It is also known that dithiourazoles may be used in internal image emulsions of the type described in Bacon et al. U.S. Pat. No. 3,447,927, issued June 3, 1969. However, improved internal image emulsions are desired which promote better maximum density and lower minimum density with minimum change when subjected to prolonged exposures of light. It would also be desirable to obtain rapid printout in emulsions with the above properties. Moreover, when photographic emulsions are chemically developed, it would be desirable to obtain improved antifoggant characteristics in the emulsion.

We have now found that image properties of photographic emulsions can be generally improved by utilizing an adduct of an α, β-unsaturated organic compound with a thiourazole. In one aspect of this invention, the emulsions contain adducts of α, β-unsaturated acids, amides, ketones aldehydes and esters with thiourazoles (including dithiourazoles). In another aspect of this invention, a diadduct is used in the emulsion which comprises 2 moles of the α, β-unsaturated compound reacted with each mole of dithiourazole. Photographic emulsions, particularly silver halide emulsions, containing the above adducts of thiourazoles exhibit unexpected improvements in photographic properties, stability, low-background fog, increased image density and the like.

In one preferred embodiment, the photographic emulsions comprise a thiourazole which is reacted with an α, β-unsaturated organic aldehyde or ketone.

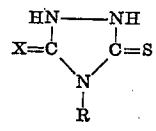
In another preferred embodiment, the photographic emulsions comprise a thiourazole which is reacted with an α, β-unsaturated acid, ester or amide.

In another embodiment, the photographic emulsions comprise dithiourazole adducts which have been further reacted with organic compounds such as hydrazines, hydroxylamine, thiosemicarbazides, semicarbazides and the like.

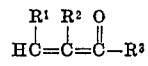
In another highly preferred embodiment, the thiourazole adducts and diadducts are used in heat-stablized printout silver halide compositions which preferably contain silver halide grains having trivalent metal ions, such as bismuth ions, occluded therein.

In another embodiment, we have found that the thiourazole adducts are preferably dissolved in an alkaline solution before addition to the photographic emulsion, especially when the thiourazole adducts are added to printout emulsions which can be heat-stabilized. Generally the thiourazole adducts of this embodiment can be dissolved in basic solutions containing alkali metal hydroxides, alkali metal carbonates or organic amines before adding them to the emulsion. Moreover, the thiourazole or dithiourazole can be mixed with the α, β-unsaturated aldehyde or ketone in an alkali medium, held for at least about one-half hour and then added to the emulsion to provide improved properties such as increased photographic speed.

Generally, the thiourazole adducts of this invention are make by the reaction of an α, β-unsaturated compound with a thiourazole of the following formula a tautomer thereof:

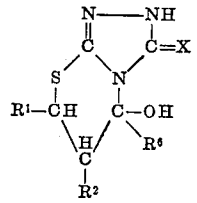


wherein X is an oxygen atom, sulfur atom or imino group and R is a hydrogen atom or an alkyl group having form ONE–eight carbon atoms such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl and the like, or an aryl group such as a phenyl group and the like. The α, β-unsaturated organic compounds preferably have the formula:



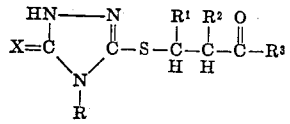
wherein R^1·R^2 can be a hydrogen atom or an alkyl group containing from about one to four carbon atoms, R^3 can be a hydrogen atom, an hydroxyl group, an amine group, an alkyl ether group or an alkyl group containing from one–10 carbon atoms.

In one embodiment of the invention, the photographic compositions comprise a reaction product of an α, β-unsaturated organic aldehyde with a thiourazole which is believed to be bicyclic and represented by the formula or a tautomer thereof:

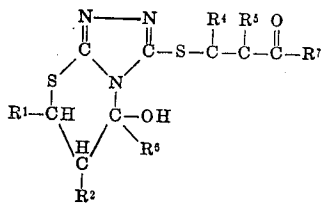


wherein X is an oxygen atom, sulfur atom, or imino group, and R^1 and R^2 are as represented above and R^6 can be a hydrogen atom or an alkyl group containing from one–10 carbon atoms.

In another embodiment, photographic compositions of this invention comprise the reaction product of an α, β-unsaturated acid, ester, ketone or amide with a thiourazole which is believed to be as follows or a tautomer thereof:



wherein R,R^1· R^2· R^3 and X are as described above. Where a dithiourazole with an Rrepresented by a hydrogen atom is reacted with the α, β-unsaturated aldehyde or ketone, it is believed that a bicyclic compound is formed when 2 molar equivalents of the α, β-unsaturated compound are used. The reaction product is believed to be as follows:



wherein R^1· R^2· R^4· R^5 andR^6 are as described above and R^7 is an hydroxyl group, an amine group, an alkyl ether group, an alkyl group having from one–10 carbon atoms. It is understood that R^1· R^2· R^4 and R^5 can each be different groups from the other.

In still another embodiment, the photographic compositions comprise the adducts and diadducts of thiourazoles and dithiourazoles which are further reacted through the remaining functional reactive groups with organic compounds such as hydrazines, oximes, semicarbazides, thiosemicarbazides and the like.

The photographic compositions of this invention intended for chemical development generally contain the thiourazole adducts in concentrations of about 0.01 mg. to about 20 g. per mole of the light-sensitive compound, and preferably from about 0.1 mg. to about 10 g.

In one preferred embodiment, silver halide emulsions according to this invention contain antifoggant concentrations of the thiourazole adduct. Where the thiourazole adduct is used in antifoggant concentrations, the preferred thiourazole adducts comprise an alkyl-carbonyl group.

In one preferred embodiment according to this invention, the thiourazole adducts have been found to be especially useful in silver halide emulsions which comprise silver halide grains having polyvalent metal ions occluded therein, especially where trivalent metal ions such as bismuth and iridium are occluded in the grains. Typical emulsions of this type are disclosed in Bacon et al. U.S. Pat. No. 3,447,927, issued June 3, 1969. Silver halide emulsions of this type can be exposed, heat-processed and photodeveloped by various procedures, such as, for example, by the procedure of Colt, U.S. Pat. No. 3,418,122 issued Dec. 24, 1968. In this embodiment, the thiourazole adducts are generally utilized in the silver halide emulsion in concentrations of up to about 100 mole percent, and preferably from about 1 mole percent to about 25 percent based on the silver.

The silver halide emulsion of a photographic element according to this invention can contain conventional addenda such as gelatin plasticizers, coating aids, antifoggants such as the azaindines and hardeners such as aldehyde hardeners, e.g., formaldehyde, mucochloric acid, glutaraldehyde bis (sodium bisulfite), maleic dialdehyde aziridines, vinyl sulfonyl ethers, dioxane derivatives and oxypolysaccharides and the like. Sensitizing dyes useful in sensitizing such emulsions are described, for example, in U.S. Pat. No. 2,526,632 of Brooker and white issued Oct. 24, 1950, and US. Pat. No. 2,503,776 of Sprague issued Apr. 11, 1950. Spectral sensitizers which can be used are the cyanines, merocyanines, complex (trinuclear) cyanines, complex (trinuclear) merocyanines, styryls and hemicyanines. Developing agents can also be incorporated into the silver halide emulsion if desired or can be contained in a separate underlayer. V arious 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. The silver halides used can be those which form latent images predominantly on the surface of the silver halide grains or those which form latent images inside the silver halide crystals such as described in U.S. Pat. No. 2,592,250 of Davey and Knott issued Apr. 8, 1952.

The silver halide emulsion layer of a photographic element which is useful in the instant invention can contain any of the hydrophilic water-permeable binding materials suitable for this purpose. Suitable materials include gelatin, colloidal albumin, polyvinyl compounds, cellulose derivatives, acrylamide polymers, etc. Mixtures of these binding agents can also be used. The binding agents for the emulsion layer of the photographic element can also contain dispersed polymerized vinyl compounds. Such compounds are disclosed, for example, in U.S. Pat. Nos. 3,142,568 of Nottorf issued July 28, 1964; 3,193,386 of White issued July 6, 1965; 3,062,674 of Houck, Smith and Yudelson issued Nov. 6, 1962; and 3,220,844 of Houck, Smith and Yudelson issued Nov. 30, 1965; and include the water-insoluble polymers and latex copolymers of alkyl acrylates and methacrylates, acrylic acid, sulfoalkyl acrylates or methacrylates and the like.

The silver halide emulsion of a photographic element which is useful in the instant invention can be coated on a wide variety of supports. Typical supports are cellulose nitrate film, cellulose ester film, polyvinyl acetal film, polystyrene film, poly(ethylene terephthalate) film, polycarbonate film and related films or resinous materials as well as glass, paper, metal and the like. Supports such as paper which are coated with α-olefin polymers, particularly polymers of α-olefins containing two or more carbon atoms, as exemplified by polyethylene, polypropylene, ethylenebutene copolymers and the like can also be employed.

The speed of the photographic emulsions useful in the instant invention can be further increased by including in the emulsions a variety of hydrophilic colloids such as carboxymethyl protein of the type described in U.S. Pat. Nos. 3,011,890 of Gates, Jr., Miller and Koller issued Dec. 5, 1961, **and polysaccharides of the type described in Canadian Pat. No.** 635,206 of Koller and Russell issued Jan. 23, 1962.

Photographic emulsions useful in the instant invention can also contain speed-increasing compounds such as quaternary ammonium compounds, polyethylene glycols or thioethers. Frequently, useful effects can be obtained by adding the aforementioned speed-increasing compounds to the photographic developer solutions instead of, or in addition to, the photographic emulsions.

The photographic elements prepared according to the instant invention can be used in various kinds of photographic systems. In addition to being useful in X-ray and other nonoptically sensitized systems, they can also be used in orthochromatic, panchromatic and infrared sensitive systems. The sensitizing addenda can be added to photographic systems before or after any sensitizing dyes which are used.

The invention can be used in emulsions intended for color photography, for example, emulsions containing color-forming couplers or emulsions to be developed by solutions containing couplers or other color-generating materials, emulsions of the mixed-packet type such as described in U.S. Pat. No. 2,698,794 of Godowsky issued Jan. 4, 1955; in silver dye-bleach systems; and emulsions of the mixed-grain type such as described in U.S. Pat. No. 2,592,243 of Carroll and Hanson issued Apr. 8, 1952.

Silver halide emulsions useful in the instant invention can be sensitized using any of the well-known techniques in emulsion making, for example, by digesting with naturally active gelatin or various sulfur, selenium, tellurium compounds and/or gold compounds. The emulsions can also be sensitized with salts of noble metals of Group VIII of the Periodic Table which have an atomic weight greater than 100.

Silver halide emulsions containing the antifoggant of the invention can be used in diffusion transfer processes which utilize the undeveloped silver halide in nonimage areas of the negative to form a positive by dissolving the undeveloped silver halide and precipitating it on a silver layer in close proximity to the original silver halide emulsion layer. Such processes are described in U.S. Pat. Nos. 2,352,014 of Rott issued June 20, 1944: 2,543,181 of Land issued Feb. 27, 1951; and 3,020,155 of Yackel, Yutzy, Foster and Rasch issued Feb. 6, 1962. The emulsions can also be used in diffusion transfer color processes which utilize a diffusion transfer of an imagewise distribution of developer, coupler or dye from a light-sensitive layer to a second layer while the two layers are in close proximity to one another.

While it is preferred to utilize the antifoggants of the invention by incorporating them directly into a photographic element, the antifoggants could also be utilized by incorporating them into a photographic developer, since image formation would still take place in the presence of the antifoggants and they would still perform their antifoggant function.

The antifogging agents of this invention can be incorporated to advantage during manufacture in silver halide emulsions representing the variations described above. Moreover, fog control in binderless silver halide films prepared by vapor deposition of silver halide on a suitable support can be achieved by coating the antifogging agents of the invention over the vapor-deposited layer of silver halide. The invention can be further illustrated by the following examples of

preferred embodiments thereof, although it will be understood that the examples are included merely for purposes of illustration and are not intended to limit the scope of the invention unless otherwise indicated.

EXAMPLE 1

3-[*s*-carboxyethylthio]-1,2,4-triazoline-5-thione

To a stirring suspension of 6.65 gms. of 1,2,4-triazolidine-3,5-dithione in 50 ml. of water is added 3.6 gms. of acrylic acid. Within 15 minutes at room temperature the solids dissolve, and after one-half hour of stirring a precipitate forms. Stirring continues for an additional one-half hour and then after chilling the suspension, the precipitate is collected. The crude product (11 grams) is then recrystallized from dilute alcohol to produce a yield of 84 percent, m.p. 204°–205° C.

EXAMPLE 2

3-[*a*-methyl-B-carboxyethylthio]-1,2,4-trizoline-5- thione

This compound is prepared in a manner similar to that described in example 1, except that acrylic acid is replaced with crotonic acid to produce a yield of 75 percent, m.p. 196–8°C. EXAMPLE 3

3-[*s*-carboxyethylthio]-4-phenyl-2,4-triazoline-5- thione

This compound is prepared in a manner similar to that described in example 1, except that 1,2,4-triazolidene-3,5dithione is replaced with 2,4-triazolidine-4-phenyl-3,5-dithione to produce a yield of 93 percent, m.p. 175–6° C.

EXAMPLE 4

3-[*s*-N,N-dimethylcarboxamidoethylthio]-4-phenyl-1,2,4-triazoline-5-thione

This compound is prepared in a manner similar to that described in example 1, except that 1,2,4,-triazolidine-3,5,-dithione is replaced with 1,2,4-triazolidine-4-phenyl-3,5-dithione and acrylic acid is replaced with N,N-dimethylacrylamide to produce a yield of 82 percent, m.p. 169–71*L* C.

EXAMPLE 5

3-[*s*-N,N-dimethylcarboxamidoethylthio]-1,2,4-triazoline-5-thione

This compound is prepared in a manner similar to that described in example 1,except that acrylic acid is replaced with N.N-dimethylacrylamide to produce a yield of 94 percent, m.p. 90–2*L* C.

EXAMPLE 6

3-[*s*-carbobutoxyethylthio]1,2,4-triazoline-5-thione

This compound is prepared in a manner similar to that described in example 1, except that acrylic acid is replaced with butylacrylate to produce a yield of 78 percent, m.p. 110–112°C.

EXAMPLE 7

3-[*s*-carboxamidoethylthio]-1,2,4-triazoline-5-thione

This compound is prepared in a manner similar to that described in example 1, except that acrylic acid is replaced with acrylamide to produce a yield of 82 percent, m.p. 208–210*BQ* C.

EXAMPLE 8

3-[*s*-methyl-*β*-carboxamidoethylthio]-1,2,4-triazoline-5-thione

This compound is prepared in a manner similar to that described in example 1, except that acrylic acid is replaced with ethylacrylate to produce a yield of 73 percent, m.p. 102–104°C.

EXAMPLE 10

1-phenyl-3,5-dithiourazole

The preparation of this prior art compound is described in "Berichte der Deutscher Chemischer Gesellschaft," 1904, Vol. 1, page 184 37th year).

EXAMPLE 11

Samples of the compounds of examples 1–10 are added to separate portions of a high-speed silver bromoiodide emulsion that is panchromatically sensitized with a cyanine dye. Each emulsion sample is coated on a cellulose acetate film support at a coverage of 459 mg. of silver and 1040 mg. of gelatin per square foot. A sample of each film coating is then exposed on an Eastman 1B sensitometer, processed for 5 minutes in Kodak DK–50 developer, fixed, washed and dried with the following photographic results.

	Fresh			2 wk. Inc., 120° F. 50% RH		
Example No. (g./mole)	Rel. speed	γ	Fog	Rel. speed	γ	Fog
Control	100	1.29	.15	34	.96	.66
1. (.09)	65	1.03	.11	43	.98	.13
2. (.09)	57	.87	.09	36	.80	.10
3. (.009)	85	1.22	.12	69	1.20	.22
4. (.09)	76	1.17	.13	58	1.10	.17
5. (.09)	67	1.15	.11	47	1.10	.15
6. (.09)	74	1.17	.12	48	1.08	.20
7. (.09)	58	1.07	.11	34	.87	.15
8. (.09)	62	1.15	.10	49	1.20	.16
9. (.09)	55	1.20	.12	44	1.12	.19
10. (.09)	83	1.43	.14	60	1.13	.28

It can be readily been from the above table that the adducts of thiourazoles according to this invention, examples 1–9, exhibit better results as antifoggants in a photographic emulsion than similar previously known compounds such as 1-phenyl dithiourazole, illustrated in example 10.

EXAMPLE 12

3-[*s*-carboxyethylthio]-1,2,4-triazoline-5-one -thione-5-one

This compound is prepared in a manner similar to that described in example 1, except that 1,2,4-triazolidine-3,5,-dithione is replaced with 1,2,4-triazolidine-3-thione-5-one to produce a yield of 90 percent with m.p. of 188–89° C.

EXAMPLE 13

A sample of a compound prepared by the procedure of example 12 is added to a high-speed silver bromoiodide emulsion that is panchromatically sensitized, coated on a cellulose acetate film support, and exposed and processed as described in example 11. The results are compared with a control sample which does not contain the compound prepared according to example 12.

	Fresh			2 Wk. Inc. 120° F. 50% RH		
Adduct of Example No. (g/mol)	Rel. Speed	γ	Fog	Rel. Speed	γ	Fog
Control	100	1.66	.15	32	.91	.77
12 (3.0)	82	1.67	.11	60	1.02	.10

The monothiourazole adduct demonstrates improved stabilization and antifoggant results.

EXAMPLE 14

To a stirred suspension of 53.2 g. (0.4 mole of dithiourazole in 400 ml. of 1:1 alcohol-water at R.T. is added 28 g. (0.4 mole) of crotonaldehyde. The suspension warms up as stirring continues and after approximately 15 minutes a clear solution

results. At the point it is advisable to warm the solution to 60°–70 C. and filter if necessary. Stirring is continued for 1 hour and then the solution is chilled and the precipitate collected and washed twice with 50 cc. of acid 1:1 alcohol-water on the funnel. After drying at 75° C. in a vacuum oven, the yield of the first crop is 47–49 g., m.p. 190°–2° C.

The combined filtrates yield a second crop of 12–13 g. m.p. 189–191°C. after concentration to approximately two-thirds of the original volume, chilling and seeding with a crystal of the first crop material. Total yield is 59–62 g. (73–77 percent).

The product may be recrystallized from 50 percent alcohol in 90115 percent yield to give material with m.p. 191–2° C.

EXAMPLE 15

3-(β-acetylethylthio)-1,2,4-triazoline-5-thione is made by adding 6.7 g. of dithiourazole to 3.5 g. of methyl vinyl ketone in 50 cc. of 50 percent aqueous ethyl alcohol. An immediate reaction occurs which is allowed to proceed with stirring for 1 hour at room temperature. The mixture is allowed to settle and is filtered with a yield of 10 g. It is then crystallized out of ethyl alcohol and dried with a yield of 8.5 g., m.p. 146.8° C. Upon recrystallization it yields an m.p. of 152.4° C.

Analysis:

Calculated—C, 35.5; H, 4.4; N, 20.7; S, 31.5

Found—C, 35.8; H, 4.2; N, 20.7; S, 31.2

EXAMPLE 16

A radiation-sensitive gelatin silver bromoiodide photographic emulsion is prepared as described in example 19 of U.S. Pat. No. 3,447,927, issued June 3, 1969. To portions of the emulsion, the halogen acceptors and aldehydes listed below are added. The emulsion samples are coated on a paper support at about 70 mg. Ag/ft².

Sample 1—containing dithiourazole hydrazine salt at 20 grams per mole and formaldehyde at 15 grams per mole

Sample 2—containing dithiourazole at 20 grams and crotonaldehyde at 20 grams per mole

Sample 3—dithiourazole-crotonaldehyde monoadduct of example 14

Samples of each coating are then exposed imagewise through a continuous density wedge for 1 second with a 500-watt lamp and then are heated on an aluminum block for 5 seconds at a block temperature of 235° C. The samples are then photodeveloped for 5 minutes at 12 cm. from two 8-watt ultraviolet lamps.

Separate sets of these processed coatings are then given the following exposures to fluorescent room lights: none (control); 24 hours; 7 days; 14 days. The following results are obtained:

	Heat—stabilized at 235° C.—exposure to fluorescent light							
	Control		24 hours		7 days		14 days	
Addenda	$D_{max.}$	$D_{min.}$	$D_{max.}$	$D_{min.}$	$D_{max.}$	$D_{min.}$	$D_{max.}$	$D_{min.}$
Sample:								
1	1.12	.20	1.22	.27	1.30	.42	1.30	.42
2	1.00	.16	1.12	.22	1.20	.41	1.21	.44
3	0.92	.08	1.15	.10	1.28	.16	1.32	.19

EXAMPLE 17

Method A: A suspension of 9.5 g. of adduct of example 15 and 3.5 g. of acrolein in 100 ml. of 50 percent ethanol is stirred at room temperature for 18 hours. The solids dissolve after one-half hour and a precipitate begins to appear after 6 hours. The suspension is chilled and the collected precipitate is recrystallized out of ethanol to yield 10.2 g. of product m.p. 126–7° C.

Calcd. for $C_9H_{13}N_3O_2S_2$:—N, 16.2

Found: —N 16.5

Method B: A suspension of 5.1 g. of monoadduct of example 15 in 40 ml. of water-ethanol (2:1) containing 1.5 g. of acrolein is stirred for one-half hour at room temperature. The solids dissolve within one-half hour with evolution of heat and a precipitate forms on cooling. The material is collected and crystallized out of ethanol to yield 5.3 g. of product m.p. 124–6° C. This material is identical by melting point, mixture melting point and IR spectra with that obtained by method A.

EXAMPLE 18

A suspension of 11.7 g. of monothiourazole and 5.6 g. of acrolein in 50 ml. of 50 percent ethanol is stirred at room temperature. After 1 hour, the solids dissolve; stirring is continued for 2 hours. At the end of this time the solution is chilled to yield 15 g. of product. Recrystallization from 50 percent ethanol yields 10 g. of material with m.p. 209–210° C.

Calcd. for $C_5H_7N_3O_2S$:—N, 24.3

Found:—N, 24.5

EXAMPLE 19

A solution of 3.0 g. of monothiourazole and 1.8 g. of crotonaldehyde in 20 ml. of 50 percent ethanol is stirred 2 hours at room temperature and then chilled. The precipitate (3.3 g.) is crystallized out of ethanol to yield product m.p. 217–8° C.

Calcd. for $C_6H_9N_3O_2S$:—C, 38.7; H, 4.8; N, 24.8; S, 16.1

Found:—C, 38.3; H, 5.2; N, 24.5; S, 16.5

EXAMPLE 20

When dithiourazole is allowed to react with 2 moles of methyl vinyl ketone in water, well cooled with ice, an almost quantitative yield of the monoadduct precipitates within a short time. This precipitate (m.p. 152–4° C.), when allowed to react in water for an additional 18 hours at room temperature with stirring, gradually dissolves to form a new compound, the diadduct (m.p. 82–4° C.) precipitated in high yields on cooling.

EXAMPLE 21

A radiation-sensitive gelatin silver bromoiodide photographic emulsion is prepared as described in example 19 of U.S. Pat. No. 3,447,927, issued June 3, 1969. To portions of the emulsion, the dithiourazole adducts listed below and a spectral-sensitizing dye at a concentration of 150 g./Ag mole are added. The emulsion samples are coated on a paper support at about 70 mg. Ag/ft². Samples of each coating are then exposed, heated at 250° C. for 5 minutes on a Teflon surface and photodeveloped with the following results.

		Photographic Results	
Adduct (g./mole of Ag)		D_{max}	D_{min}
A	(15)	.86	.16
B	(15)	.70	.12
C	(34)	1.30	.05
D	(15)	1.20	.14
E	(15)	1.12	.08
F	(34)	1.04	.07
G	(34)	1.16	.04
H	(34)	1.13	.04
I	(46)	1.09	.04

A—3-[*s*-carboxamido-β-methylethylthio]-1,2,4-triazoline-5-thione
B—3-[*s*-carbobutoxyethylthio]-1,2,4-triazoline-5-thione
C—3-(β-acetylethylthio)-1,2,4-triazoline-5-thione
D—6,7-dihydro-5-hydroxy-s-triazolo[3,4-b]-[1,3]-thiazine-3-[2H, 5H]thione
E—3-(carbethoxyethylthio)-1,2,4-triazoline-5-thione
F—3[*s*-carboxyethylthio]-1,2,4-triazoline-5-thione
G—3(β-acetylethylthio)-6,7-dihydro-5-hydroxy-5methyl-[5H]-s-triazolo[3,4-b][1,3]-thiazine
H—3-[*s*-carboxyethylthio]-4-hydroxy-1,2,3a-triaza-7-thia-4,5,6-trihydroindene
I—3-[*s*-acetylethylthio]-4-hydroxy-6-methyl-1,2,3a-triaza-7-thia-4,5,6-trihydroindene

EXAMPLE 22

The thiourazole adducts are preferably dissolved in a n alkaline medium before addition to silver halide emulsions. A radiation-sensitive gelatin silver bromoiodide photographic emulsion is prepared as described in example 19 of U.S. Pat. No. 3,447,927, issued June 3, 1969. Thiourazole adducts are added to the emulsion at 20 grams per mole along with the spectral-sensitizing dye 3-ethyl-5-[(3-ethyl-2-benzothiazolinylidene)-1-methylidene]-2-thio-2,4-oxazolidinedione at a concentration of 150 milligrams per mole of silver. The emulsion is coated and after exposure is heated on an aluminum block for 5 seconds at a temperature of 235° C. and then photodeveloped. The thiourazole adducts are added under the following conditions:

Sample 1 - An adduct prepared according to example 14 is dissolved in methanol and added to the emulsion which is coated at a pH of 5.0.

Sample 2 - An adduct prepared according to example 14 is dissolved in methanol and added to the emulsion which is then adjusted to a coating pH of 6.5 with sodium hydroxide.

Sample 3 - An adduct prepared according to example 14 is dissolved in water and the pH adjusted to 11.4 with sodium hydroxide before adding it to the emulsion which is coated at a pH of 6.5.

Sample 4 - Dithiourazole and crotonaldehyde are mixed in equal weight portions in water and adjusted to a pH of 11.4 with sodium hydroxide and held for about one-half hour before adding it to the emulsion at a concentration of 40 grams per mole of silver which is then coated at a pH of 6.5.

Sample 5 - An adduct prepared according to example 15 is dissolved in water and the pH adjusted to 11.4 with sodium hydroxide and held for about 1 hour. The above adduct (or equilibrium product) is added to the emulsion at a concentration of 25 grams per mole of silver and is then coated at a pH of 6.5.

Sample	D_{min}	Photographic Results γ	Rel. Speed
1	0.10	0.40	100
2	0.10	0.50	132
3	0.09	0.74	501
4	0.12	0.63	631
5	0.06	0.80	631

It is apparent from the above table that the dissolution of the dithiourazole compounds with α, β-unsaturated compounds in an alkaline solution before addition to the emulsion provides a significant improvement in photographic properties such as photographic speed.

Similar improved results are obtained when the adducts of crotonaldehyde and dithiourazole, acrolein and dithiourazole, and acrylic acid with monothiourazole are substituted in the preparation of example 5. Moreover, similar improvements are obtained when the alkaline solutions above are dried down and the solids are redissolved in water before addition to the emulsion.

EXAMPLE 23

The oxime of 3-γ-ketobutylthio-1,2,4-triazoline-5-thione is prepared by dissolving 10.15 g. of the adduct prepared by the procedure of example 15 in 100 cc. of 50 percent aqueous ethyl alcohol. 3.5 g. of hydroxyl amine hydrochloride and 4.1 g. of anhydrous sodium acetate in 50 cc. of water are added and mixed. Reaction commences immediately, after which the product is settled, chilled and collected. Yield is 10 g. m.p. 194.0–195°C.

Analysis for $C_6H_{10}ON_4S_2$
Calcd.:—N, 25.7
Found:—N, 25.7

EXAMPLE 24

10.15 g. of the adduct prepared according to example 15 are dissolved in 50 cc. of 50 percent aqueous ethyl alcohol. 5.25 g. of 4-methyl-3-thiosemicarbazide in 50 cc. of 50 percent aqueous ethyl alcohol are added. After reaction, the product is settled, chilled and filtered with a yield of 15 g. at m.p. of 187°–189° C.

Analysis for $C_8H_{14}N_6S_3$
Calcd.:—N, 29.0
Found: —N, 28.6

EXAMPLE 25

10.1 g. of the adduct prepared according to example 15 are dissolved in 100 cc. of 50 percent ethyl alcohol and reacted with phenyl hydrazine at boiling temperature for one-fourth delete hour. The precipitate yields 8 g. of product with m.p. of 155° C.

Analysis for $C_{12}H_{15}N_5S_2$
Calcd.: —N, 23.9
Found: —N, 23.7

EXAMPLE 26

The dithiourazole adducts which are reacted further through the functional groups are also useful in photographic systems. The following triazoline derivatives are added to a photographic system similar to that described in example 11 with the following antifoggant and stabilization results.

Compound (g./mole)	Fresh			2 wk. inc., 120° F./50% RH		
	Relative speed	γ	Fog	Relative speed	γ	Fog
Control	100	1.41	.16	35.5	.99	.72
A. (.09)	82	1.17	.11	71	1.18	.29
B. (.09)	71	1.27	.10	62	1.17	.34
C. (.009)	85	1.38	.11	74	1.30	.15
D. (3.0)	91	1.72	.11	59	1.15	.17
E. (.06)	118	1.55	.10	62	1.20	.27
F. (.03)	120	1.68	.10	67	1.30	.18
G. (.12)	102	1.45	.15	24	.83	.26
H. (.15)	95	1.48	.12	52	1.00	.25
I. (.75)	91	1.43	.11	73	1.03	.15
J. (.15)	74	1.40	.14	71	1.25	.22
K. (.15)	71	1.25	.12	80	1.22	.19
L. (.75)	53	1.10	.14	33	.88	.17
M. (.09)	60	1.43	.13	52	1.13	.15

A—Oxime of 3-γ-ketobutylthio-1,2,4-triazoline-5-thione
B—Semicarbazone of 3-γ-ketobutylthio-1,2,4-triazoline-5-thione
C—Phenylhydrazone of 3-[*d*-ketobutylthio]-1,2,4-triazoline-5-thione
D—3(β-carboxyethylthio-4-methyl-1,2,4-triazoline-5-one
E—3-(γ-ketobutylthio)-4-methyl-1,2,4-triazoline-5-one
F—3-(γ-ketobutylthio)-4-methyl-1,2,4-triazoline-5-thione
G—4-hydroxy-4,5,6,7-tetrahydro-7-thia-1,2,3a-triazaindene -3-thione

H—6,7-dihydro-5-hydroxy-3(γ-ketobutylthio)-7-methyl-[5H]-s-triazolo[3,4-b][1,3]-thiazine
I—3-(β-acetylethylthio)-6,7-dihydro-5-hydroxy-6-methyl[5-H]-s-triazolo[3,4-b][1,3]-thiazine
J—3-carbethoxyethylthio-6,7-dihydro-5-hydroxy-5-methyl-[5-H]-s-triazolo[3,4-b][1,3]-thiazine
K—3-(carbethoxyethylthio)-6,7-dihydro-5-hydroxy-[5H]-s-triazolo-[3,4-b][1,3]-thiazine
L—3-(γ-ketobutylthio)-5-oxo-1,2,4-triazolidine
M—3-(α-methyl-β-carbethoxyethylthio)-1,2,4-triazoline-5-thione

EXAMPLE 27

The thiourazole adducts are advantageously used in color photographic systems as antifoggants.

The thiourazole derivatives listed in the following table are added to separate portions of a red-sensitive sulfur and gold-sensitized gelatin-silver bromoiodide emulsion containing a dispersion of a cyan-forming phenolic coupler of the type described in U.S. Pat. No. 2,474,293 as Compound 1. The emulsion samples and a control are coated on a cellulose acetate film support at 100 mg. Ag/ft.^{2} and 272 mg. gelatin/ft.^{2}. A sample of each film coating is exposed on an Eastman 1B sensitometer and processed in the Eastman Color Negative Process C-22 (12′ development). The results in the following table illustrate the antifoggant and stabilization advantage obtained from the use of thiourazole adducts.

	Fresh			1 wk. incubation		
Compound (g./Ag mole)	Rel. speed	γ	Fog	Rel. speed	γ	Fog
	100	1.22	.12	91	.85	.24
A. (.02)	89	1.15	.11	85	.98	.14
B. (.06)	91	1.27	.05	94	.98	.11
C. (.02)	74	1.05	.07	74	.77	.13
D. (.036)	65	1.03	.05	95	.91	.11
E. (.18)	91	1.12	.07	105	.92	.13
F. (.045)	50	.87	.04	71	.85	.14
G. (.03)	62	1.13	.06	123	1.12	.16

A—3-[s-carboxyethylthio]-1,2,4-triazoline-5-thione
B—3-[s-N,N-dimethylcarboxamidoethylthio]-4-phenyl-1,2,4-triazoline-5-thione
C—3-[s-methyl-β-carboxyethylthio]-1,2,4-triazoline-5-thione
D—3-[s-methyl-β-carbomethoxyethylthio]-1,2,4-triazoline-5-thione
E—3-(2-acetylethylthio)-4-phenyl-1,2,4-triazole-5-thione
F—Oxime of 3-γ-ketobutylthio-1,2,4-triazoline-5-thione
G—3-(β-methyl-β-carbethoxyethylthio)-1,2,4-triazoline-5-thione

EXAMPLE 28

Vinyl sulfonyl ethers are preferably used as hardeners in combination with the thiourazole adducts in photographic emulsions containing hydrophilic colloids such as gelatin.

A radiation-sensitive gelatino-bromoiodide (6 mole percent iodide) emulsion precipitated in the presence of bismuth ions according to Bacon et al. U.S. Pat. No. 3,447,927 is coated on a paper support at 60 mg. Ag/ft.^{2} and 550 mg. gelatin/ft.^{2}. To the emulsion is added bis(vinyl sulfonylmethyl)ether at 2.4 g./silver mole and an alkaline solution (pH 11.2) of 3-(1thiapentan-4-one)-1,2,4-triazoline-5-thione at 34 g./silver mole. The hardened coating is then processed by the following steps.

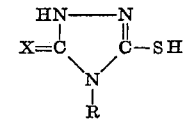
1. exposing one-tenth second on an Eastman 1B sensitometer through a 0.15 *FD* step wedge;
2. heating at 235° C. for 4 seconds on a hot platen; and
3. photodeveloping 5 minutes at 6 inches from a No. 2 reflector photoflood lamp.

The processed coating exhibits 16 steps with a maximum density of 1.27 and a minimum density of 0.09.

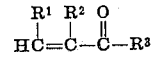
Although the invention has been described in considerable detail with particular reference to certain preferred embodiments thereof, variations, and modifications can be effected within the spirit and scope of the invention.

We claim:

1. A photographic composition comprising a silver halide emulsion and an antifoggant concentration of an adduct of a thiourazole compound of the following formula or a tautomer thereof:



wherein X can be an oxygen atom, sulfur atom, or an imino group, and R is a hydrogen atom, an alkyl group having from one to eight carbon atoms, or a phenyl group; with an α, β-unsaturated organic compound having the formula:



wherein R^1 and R^2 can be a hydrogen atom or an alkyl group containing from one to four carbon atoms, and R^3 can be a hydrogen atom, a hydroxyl group, an amine group, an alkyl ether group having from one to 10 carbon atoms, or an alkyl group having from one to 10 carbon atoms.

2. A photographic composition according to claim 1 wherein said α, β-unsaturated organic compound is an aldehyde or ketone.

3. A photographic composition according to claim 1 wherein said α, β-unsaturated organic compound is an acid, ester, or amine.

4. A photographic composition according to claim 1 wherein X is a sulfur atom.

5. A photographic composition according to claim 1 wherein said adduct is a diadduct wherein X is a sulfur atom and R is a hydrogen atom.

6. A photographic composition according to claim 1 wherein said α, β-unsaturated compound is crotonaldehyde.

7. A photographic composition according to claim 1 wherein said α, β-unsaturated compound is methyl vinyl ketone.

8. A photographic composition according to claim 1 wherein said adduct is a diadduct of dithiourazole with crotonaldehyde, methyl vinyl ketone, or a mixture thereof.

9. A composition according to claim 1 wherein said adduct is 3(β-acetylethylthio-1,2,4-triazoline-5-thione.

10. A composition according to claim 1 wherein said adduct is 3[-acetylethylthio)-1,2,4-triazoline-5-thione. -acetylethylthio]-6,7-dihydro-5-hydroxy-5-methyl-5H-s-triazolo[3,4-b][1,3]-thiazine.

11. A photographic composition according to claim 1 which further comprises a hydrophilic colloid and a vinyl sulfonyl ether hardener.

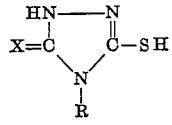
12. A process for preparing a photographic composition as set forth in claim 1 which comprises dissolving said adduct in an alkaline medium and then adding it to the silver halide emulsion.

13. A process for preparing a photographic composition as set forth in claim 1 which comprises mixing the thiourazole with the α, β-unsaturated compound in an alkali medium so as to obtain an adduct and then adding it to a photographic emulsion.

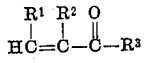
14. A photographic composition according to claim 1 wherein said adduct is present in a concentration of from about 0.01 mg. to about 20 grams per mole of silver.

15. A photographic composition according to claim 1 wherein said adduct is present in a concentration of from about 0.1 mg. to about 10 grams per mole of silver.

16. A light-developable direct-print photographic composition comprising a silver halide emulsion in which the silver halide grains have trivalent metal ions occluded therein, and from about 1 to 100 mole percent, based on the silver, of an adduct of a thiourazole compound of the following formula or a tautomer thereof:



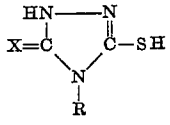
wherein X can be an oxygen atom, sulfur atom, or an imino group, and R is a hydrogen atom, an alkyl group having from one to eight carbon atoms, or a phenyl group; with an α,β-unsaturated organic compound having the formula:



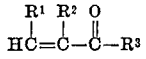
wherein R^1 and R^2 can be a hydrogen atom or an alkyl group containing from one to four carbon atoms, and R^3 can be a hydrogen atom, a hydroxyl group, an amine group, an alkyl ether group having from one to 10 carbon atoms, or an alkyl group having from one to 10 carbon atoms.

17. A composition according to claim 16 wherein said trivalent metal ions are bismuth ions, and said adduct is present in a concentration of from about 1 to about 25 mole percent, based on the silver.

18. A photographic element comprising a support, a silver halide layer, and as an addendum, an antifoggant concentration of an adduct of a thiourazole compound of the following formula or a tautomer thereof:

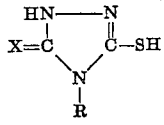


wherein X can be an oxygen atom, sulfur atom, or an imino group, and R is a hydrogen atom, an alkyl group having from one to eight carbon atoms, or a phenyl group; with an α,β-unsaturated organic compound having the formula:

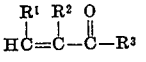


wherein R^1 and R^2 can be a hydrogen atom or an alkyl group containing from one to four carbon atoms, and R^3 can be a hydrogen atom, a hydroxyl group, an amine group, an alkyl ether group having from one to 10 carbon atoms, or an alkyl group having from one to 10 carbon atoms.

19. A photographic element comprising a support, a silver halide layer having trivalent metal ions occluded in the silver halide grains thereof, and from about 1.0 to about 25 mole percent, based on the silver, of an adduct of a thiourazole compound of the following formula or a tautomer thereof:



wherein X can be an oxygen atom, sulfur atom, or an imino group, and R is a hydrogen atom, an alkyl group having from one to eight carbon atoms, or a phenyl group; with an α,β-unsaturated organic compound having the formula:



wherein R^1 and R^2 can be a hydrogen atom or an alkyl group containing from one to four carbon atoms, and R^3 can be a hydrogen atom, a hydroxyl group, an amine group, an alkyl ether group having from one to 10 carbon atoms, or an alkyl group having from one to 10 carbon atoms.

* * * * *

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,615,618 Dated October 26, 1971

Inventor(s) Albert W. Wise, John W. Gates, Jr., Dorothy J. Beavers

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 69, after "formula", please insert---or---. Column 2, line 2, "form" should read ---from---. Column 3, line 41, "white" should read ---White---; line 48, "V arious" should read ---Various---. Column 4, line 47, "antifoggant" should read ---antifoggants---. Column 5, line 8, "3-[s-carboxyethylthio]-1,2,4-triazoline-5-thione" should read ---3-[β-carboxyethylthio]-1,2,4-triazoline-5-thione---; line 27, "triazolidene" should read ---triazolidine---; line 33, "3-[s-N,N-dimethylcarboxamidoethylthio]-4-phenyl-1,2,4-triazoline-5-thione" should read ---3-[β-N,N-dimethylcarboxamidoethylthio]-4-phenyl-1,2,4-triazoline-5-thione---; line 39, "169-71LC" should read ---169-71°C---; line 42, "3-[s-N,N-dimethylcarboxamidoethylthio]-1,2,4-triazoline-5-thione" should read ---3-[β-N,N-dimethylcarboxamidoethylthio]-1,2,4-triazoline-5-thione---; line 46, N.N-dimethylacylamide" should read ---N,N-dimethylacylamide---; line 47, "90-2LC" should read ---190-2°C; line 51, "3-[s-carbobutoxyethylthio]-1,2,4-triazoline-5-thione" should read ---3-[β-carbobutoxyethylthio]-1,2,4-triazoline-5-thione---; line 59, "3-[s-carboxamidoethylthio]-1,2,4-triazoline-5-thione" should read ---3-[β-carboxamidoethylthio]-1,2,4-triazoline-5-thione---; line 63, "208-210BQC" should read ---208-210°C.---; line 66, "3-[s-methyl-β-carboxamidoethylthio]-1,2,4-triazoline-5-thione" should read ---3-[β-methyl-β-carboxamidoethylthio]-1,2,4-triazoline-5-thione---. Column 6, line 40, "3-[s-carboxyethylthio]-1,2,4-triazoline-5-one -thione-5-one" should read ---3-[β-carboxyethylthio]-1,2,4-triazoline-5-one---; line 72, after "mole", please insert ---)---. Column 7, line 13, "90115" should read ---90+---. Column 9, line 1, "3-[s-carboxamido-β-methylethylthio]-1,2,4-triazoline-5-thione" should read ---3-[β-carboxamido-β-methylethylthio]-1,2,4-triazoline-5-thione---;

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,615,618 Dated October 26, 1971

Inventor(s) Albert W. Wise, John W. Gates, Jr., Dorothy J. Beavers

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 9, line 3, "3-[s-carbobutoxyethylthio]-1,2,4-triazoline-5-thione" should read ---3-[β-carbobutoxyethylthio]-1,2,4-triazoline-5-thione---; line 8, "3-[s-carboxyethylthio]-1,2,4-triazoline-5-thione" should read ---3-[β-carboxyethylthio]-1,2,4-triazoline-5-thione---; line 11, "3-[s-carboxyethylthio]-4-hydroxy-6-methyl-1,2,3a-triaza-7-thia-4,5,6-trihydroindene" should read ---3-[β-carboxyethylthio]-4-hydroxy-6-methyl-1,2,3a-triaza-7-thia-4,5,6-trihydroindene---; line 13, "3-[s-acetylethylthio]-4-hydroxy-6-methyl-1,2,3a-triaza-7-thia-4,5,6-trihydroindene" should read ---3-[β-acetylethylthio]-4-hydroxy-6-methyl-1,2,3a-triaza-7-thia-4,5,6-trihydroindene---; line 62, in Sample 2, "0.50" should read ---0.54---. Column 10, line 15, "194.0-195°C" should read ---194.5°C---; line 27, "187-189°C" should read ---187.9°C---; line 36, before "hour", please delete the word ---delete---; line 69, "Phenylhydrazone of 3-[d-ketobutylthio]-1,2,4-triazoline-5-thione" should read ---Phenylhydrozone of 3-[γ-ketobutylthio]-1,2,4-triazoline-5-thione---. Column 11, line 40, "3-[s-carboxyethylthio]-1,2,4-triazoline-5-thione" should read ---3-[β-carboxyethylthio]-1,2,4-triazoline-5-thione---; line 41, "3-[s-N,N-dimethylcarboxamidoethylthio]-4-phenyl-1,2,4-triazoline-5-thione" should read ---3-[β-N,N-dimethylcarboxamidoethylthio]-4-phenyl-1,2,4-triazoline-5-thione---; line 43, "3-[s-methyl-β-carboxyethylthio]-1,2,4-triazoline-5-thione" should read ---3-[β-methyl-β-carboxyethylthio]-1,2,4-triazoline-5-thione---; line 45, "3-[s-methyl-β-carbomethoxyethylthio]-1,2,4-triazoline-5-thione" should read ---3-[β-methyl-β-carbomethoxyethylthio]-1,2,4-triazoline-5-thione---; line 66, "FD" should read ---ΔD---. Claim 10, "3-[-acetylethylthio)-1,2,4-triazoline-5-thione.acetylethylthio]-6,7-dihydro-5-hydroxy-5-methyl-5H-s-triazolo[3,4-b][1,3]-thiazine." should read ---3-[β-acetylethylthio]-6,7-dihydro-5-hydroxy-5-methyl-5H-s-triazolo[3,4-b][1,3]-thiazine---.

Signed and sealed this 1st day of August 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents