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3,598,598 FOG STABILIZERS FOR PHOTOGRAPHIC EMULSIONS

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U.S. Cl. 96—109

20 Claims

ABSTRACT OF THE DISCLOSURE

A photographic silver halide emulsion or photographic element containing a fog-stabilizing amount of a thionamide, e.g., a 3-substituted thiazoline-2-thione, N,N-disubstituted dithiocarbamic ester or an N,N,N',N'-tetrasubstituted thiourea, which contains at least one acid group in the molecule is disclosed. The acid group or groups contained in the thionamide molecule should be ones which will confer a negative charge to the thione at a pH of 5 or below and is exemplified by carboxylic or sulfonic acid groups. Silver halide complexes of thionamides and developing photographic elements are also described.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to new and improved antifog-
gants and stabilizers for photographic elements and to
photographic silver halide emulsions containing said
antifoggants and stabilizers therein. The invention also
relates to silver halide complexes and to a process of
developing photographic elements in the presence of new
and improved antifoggants.

Description of the prior art

During development of a silver halide emulsion, small
amounts of silver halide are reduced to metallic silver
regardless of whether or not they have been exposed.
This reduction of silver ion produces a background fog
which is more specifically referred to as chemical fog.

Chemical fog, apparent in most silver halide systems,
has been reduced by prior art methods of processing ex-
posed silver halide material in the presence of compounds
which restrict development of unexposed silver halide.
Such compounds can be incorporated in the silver halide
emulsion or in the processing solutions for developing
such silver halide emulsions. Compounds which have
been found to have a chemical fog inhibiting effect on
emulsions which have been subjected to high tempera-
ture and high humidity conditions are referred to as emul-
sion stabilizers. On the other hand, compounds which
have been found to have chemical fog inhibiting effects
on emulsions which have not been exposed to adverse
storage conditions are referred to as antifoggants. Al-
though a large number of emulsion stabilizers and anti-
foggants have been used in the prior art, many of these
compounds cause undesirable losses in emulsion speed
and contrast and others lack adequate compatibility with
emulsion gelatin.

Thionamides have been used in the past as antifoggants
in silver halide emulsions. Such compounds generally
contain at least one hydrogen atom on the amidic nitro-
gen and exist in tautomeric equilibria between the thione
and sulfhydryl structure. However, these compounds
have a propensity to desensitize fast silver halide emul-
sions and, therefore, are generally used in concentrations
of less than 50 milligrams per mole of silver to prevent
objectionable loss of emulsion sensitivity.

SUMMARY OF THE INVENTION

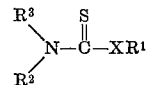
According to one embodiment of this invention, there
is incorporated into the silver halide emulsion of a photo-
graphic element or in a layer contiguous to the silver
halide emulsion, a fog stabilizing amount of an acrylic
or monocyclic thionamide, said thionamide containing at
least one acid group which will confer a negative charge
to the thionamide at a pH of 5 or below. These com-
pounds stabilize the emulsion against fog when the dried
emulsion has been subjected to a prolonged high humidity
and temperature incubation period without adversely ef-
fecting other sensitometric properties.

According to another embodiment of the invention, a
photographic element comprising a support coated with
at least one silver halide emulsion layer is developed in
the presence of one of the previously described thiona-
mides. Preferably, the thionamide is present in the photo-
graphic element but it can be present elsewhere in the
system—e.g., in the developer.

According to still another embodiment of this inven-
tion, there are provided water- or alkali-soluble silver
complexes of the previously described thionamides.

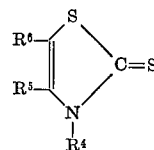
DESCRIPTION OF THE PREFERRED EMBODIMENT

Thionamides which are suitably used in the practice
of this invention include those having the general for-
mula



wherein X represents sulfur, oxygen or an iso-electronic
group, e.g., $-\text{CH}=\text{CH}-$ (where R^1 and R^2 are taken to-
gether) or $=\text{NR}$ where R is an aliphatic group or a
substituted aliphatic group, R^1 , R^2 and R^3 , when taken
separately, are aliphatic groups or substituted aliphatic
groups, R^1 and R^2 , when taken together, represent an
alkylene group, and R^2 and R^3 , when taken together with
the nitrogen atom to which they are attached, repre-
sent a heterocyclic group, at least one of the groups con-
taining an acid substituent.

One group of thionamides which can be used in the
practice of this invention are 3-substituted thiazoline-2-
thiones which have the structure



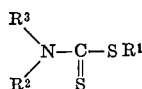
wherein R^4 is an aliphatic group, e.g., an alkyl chain
containing up to 10 carbon atoms which can be sub-
stituted with one or more groups such as carboxyl, sul-
fonyl, etc.; R^5 and R^6 can each be hydrogen, an aliphatic
or substituted aliphatic radical, e.g., a keto group, a car-
boxyl group or an alkyl group containing up to 10 car-
bon atoms, which alkyl group can be further substituted
with one or more other groups such as carboxyl, sulfonyl,
hydroxy, an ester group, etc.; and at least one of R^4 , R^5
and R^6 contains an acid substituent such as a carboxylic
or sulfonic acid group. Compounds having the above
structure which can be used in the practice of this inven-

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tion are set forth below wherein the groups R^4 , R^5 and R^6 are as specified:

R^4	R^5	R^6
$-\text{CH}_2\text{CO}_2\text{H}$	$-\text{C}_6\text{H}_5$	$-\text{H}$
$-\text{CH}_2\text{CO}_2\text{H}$	$-\text{CH}_3$	$-\text{CO}_2\text{CH}_2\text{CH}_3$
$-\text{CH}_2\text{CO}_2\text{H}$	$-\text{CH}_3$	$-\text{CO}_2\text{H}$
$-\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$	$-\text{H}$	$-\text{H}$
$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CHCO}_2\text{H} \end{array}$	$-\text{CH}_3$	$-\text{C}(=\text{O})\text{CH}_3$
$-\text{CH}_2\text{CH}_2\text{SO}_3\text{H}$	$-\text{CH}_3$	$-\text{H}$
$-\text{CHCO}_2\text{H}$	$-\text{CH}_3$	$-\text{CH}_3$
$\begin{array}{c} \text{CH}_2\text{CO}_2\text{H} \\ \\ -\text{CH}_3 \end{array}$		
$-\text{CH}_3$	$-\text{CH}_3$	$-\text{CO}_2\text{H}$
$-\text{CH}_3$	$-\text{CH}_2\text{CO}_2\text{H}$	$-\text{H}$

Another group of thionamides which can be used in the practice of this invention are N,N-disubstituted di-thiocarbamic esters having the structure



wherein R^1 , R^2 and R^3 are the same as defined above. Thus, the group



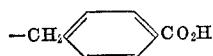
can be



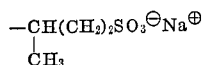
or a heterocyclic ring having 4 or 5 carbon atoms such as



and R^1 can be a substituted aliphatic group having from 3 to 10 carbon atoms and containing a carboxylic or sulfonic acid group such as



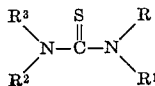
or



Examples of such compounds include the following wherein the variable groups are as indicated:

$\begin{array}{c} R^3 \\ \\ R^2 - N - \\ \\ R^1 \end{array}$	
$\begin{array}{c} \text{CH}_3 \\ \\ -N- \\ \\ \text{CH}_3 \end{array}$	$-\text{CH}_2-\text{C}_6\text{H}_4-\text{CO}_2\text{H}$
$\begin{array}{c} \text{CH}_3\text{CH}_2 \\ \\ -N- \\ \\ \text{CH}_3\text{CH}_2 \end{array}$	Same as above.
$\begin{array}{c} \text{CH}_3\text{CH}_2 \\ \\ \text{O} \end{array}$	Do.
$\begin{array}{c} \text{---} \text{N} \text{---} \\ \\ \text{O} \end{array}$	$-(\text{CH}_2)_4\text{SO}_3^-\text{Na}^+$

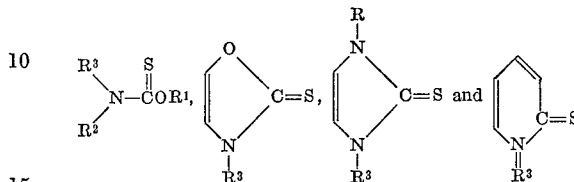
A further group of thionamides which can be used are N,N,N',N'-tetrasubstituted thioureas having the structure



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wherein R , R^1 , R^2 and R^3 are the same as defined above. These groups can be, for example, hydrocarbon residues having from 1 to 10 carbon atoms, at least one of the groups containing an acid substituent such as a carboxylic or sulfonic acid group.

Other groups of thionamides which can be used include those having the general formulas



wherein R , R^1 , R^2 and R^3 are the same as previously defined.

The thionamide can be incorporated into the silver halide emulsion of a photographic element or in a layer contiguous to the silver halide emulsion in any amount which will stabilize the silver halide emulsion against fog. In general, a concentration of the thionamide in an amount of from about 0.05 to about 30, preferably about 0.6 to about 10.0 grams per mole of silver in the silver halide emulsion can be used with good results.

The preparation of photographic silver halide emulsions such as are suitably stabilized with the thionamide typically 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 increase demulsion speed or sensitivity. (Mees, "The Theory of the Photographic Process," 1954.) The thionamide can be added to the emulsion before the final digestion or after-ripening or it can be added immediately prior to the coating.

The silver halide emulsion of a photographic element containing the antifoggants of this invention can contain conventional addenda such as gelatin plasticizers, coating aids, and hardeners such as aldehyde hardeners, e.g., formaldehyde, mucochloric acid, glutaraldehyde bis(sodium bisulfite), maleic dialdehyde, aziridines, dioxane derivatives and oxypolysaccharides. Spectral sensitizers which can be used are the cyanines, merocyanines, complex (trinuclear) cyanines, complex (trinuclear) merocyanines, styryls, and hemicyanines. Sensitizing dyes useful in sensitizing such emulsions are described, for example, in U.S. Pats. 2,526,632 of Brooker and White issued Oct. 24, 1950, and 2,503,776 of Sprague issued Apr. 11, 1950. Developing agents can also be incorporated into the silver halide emulsion if desired or can be contained in a contiguous layer. 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, silver bromoiodide and the like. 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. 2,592,250 of Davey and Knott issued Apr. 8, 1952.

The silver halide emulsion layer of a photographic element containing the antifoggants of the 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. Pats. 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 of alkyl acrylates

and methacrylates, acrylic acid, sulfoalkyl acrylates or methacrylates and the like.

The silver halide emulsion of a photographic element containing the antifoggants of the 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 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 sensitometric characteristics of the photographic emulsions containing the antifoggants of the invention can be further enhanced by including in the emulsions a variety of hydrophilic colloids such as carboxymethyl protein of the type described in U.S. Pat. 3,011,890 of Gates, Jr., Miller and Koller issued Dec. 5, 1961, and polysaccharides of the type described in Canadian Pat. 635,206 of Koller and Russell issued Jan. 23, 1962.

Photographic emulsions containing the antifoggants of the 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.

Photographic elements containing the antifoggants of the instant invention can be used in various kinds of photographic systems. In addition to being useful in X-ray and other non-optically 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.

Silver halide emulsions containing the antifoggants of the invention can be used in 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. Patent 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. 2,592,243 of Carroll and Hanson issued Apr. 8, 1952.

Silver halide emulsions containing the antifoggants of the 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 antifoggants of the invention can be used in diffusion transfer processes which utilize the undeveloped silver halide in non-image areas of the negative to form a positive by dissolving the undeveloped silver halide and precipitating it on a receiving layer in close proximity to the original silver halide emulsion layer. Such processes are described in U.S. Patents 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. Silver halide emulsions containing the antifoggants of the invention can be processed in stabilization processes such as the ones described in U.S. Pat. 2,614,927 of Broughton and Woodward issued Oct. 21, 1952, and as described in the article "Stabilization Processing of Films and Papers" by H. D. Russell, E. C.

Yackel and J. S. Bruce in P.S.A. Journal, Photographic Science and Technique, volume 16B, October 1950.

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 to control development fog.

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.

Combinations of all the above-mentioned addenda can be used if desired.

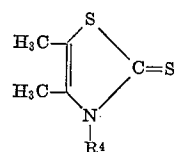
While the antifoggant action of the thionamide compounds of this invention are particularly advantageous, their ability to complex with metal ions, especially with silver ions, warrants their use in numerous photographic systems. Thus, they can be utilized in silver halide diffusion transfer systems; as silver halide grain growth agents to promote Ostwald ripening; as fixing agents; and as stabilization agents for unexposed silver halide in stabilization processing systems as described, for example, in Broughton et al. U.S. Patent 2,614,927 issued October 21, 1952. The thiones of this invention can also be used to form intramolecular salts or chelates with silver ions which, when coated in a suitable binder on a suitable support form light-sensitive layers as described in copending application Ser. No. 764,298 of Haist et al. entitled Photosensitive Compositions Comprising Silver Complexes of 3-Substituted-4-Thiazoline-2-Thiones and Photosensitive Elements Comprising Such Compositions filed concurrently herewith. The stability of these silver complexes will withstand extreme keeping conditions permitting their incorporation into photographic elements as a silver source for physical development and used, for example, in systems of the type described in Agfa British Pat. 920,277 issued Mar. 6, 1963; Kodak Belgian Pat. 672,283 issued Mar. 1, 1966; and copending application Ser. No. 764,330 of Bass entitled Photographic Element, Composition and Process filed concurrently herewith. The dual properties of stability and light sensitivity of these silver-thione complexes allow them to be utilized with light-sensitive catalysts, which can or cannot be photoconductors, in a bifunctional photographic element containing two light-sensitive components which can be treated selectively to produce two independent images. Alternatively, these silver complexes can be utilized in image reproduction systems in combination with a reducing agent and a light-sensitive catalyst as described in Shepard et al. U.S. Pat. 3,152,903 issued Oct. 13, 1964.

The invention can be further illustrated by the following examples or preferred embodiments thereof, although it will be understood that these examples are included merely for purposes of illustration and are not intended to limit the scope of the invention.

In the following examples, the stabilizer compound is neutralized by the addition of a base before addition to the emulsion where it is necessary to maintain the pH of the emulsion constant.

EXAMPLE 1

Photographic emulsions are prepared by adding thionamides having the formula



wherein R^4 is defined in Table 1, to separate portions of a high speed gold and sulfur sensitized bromiodide emul-

sion. Each emulsion sample is coated on a cellulose acetate film support at a coverage of 350 milligrams of silver

50 at 68° F. for five minutes. The photographic results are set forth in Table 2.

TABLE 2

Stabilizer compound		Fresh		2 week incubation at 120° F. and 50% relative humidity	
R ⁴	g./mole Ag	Relative speed	Fog	Relative speed	Fog
Control.....		100	0.10		0.66
-CH ₂ CO ₂ H.....	3.0	102	0.09	107	0.12
-CH ₂ CH ₂ CO ₂ H.....	3.0	105	0.10	118	0.15
-CH ₂ CH ₂ CH ₂ CO ₂ H.....	3.0	105	0.17	110	0.28

and 840 milligrams of gelatin per square foot. A sample of each film coating is exposed on an intensity scale sensitometer, processed for four minutes at 68° F. in Kodak Developer D-19, fixed, washed and dried. The photographic results obtained from these tests are listed in Table 1.

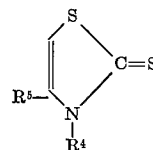
TABLE 1

Thionamide, R ₄	G./mole Ag	Fresh		2 week incubation at 120° F. and 50% relative humidity, fog
		Relative speed	Fog	
Control.....		100	0.09	0.39
-CH ₃	0.048	97	0.10	>1.0
-CH ₂ CO ₂ H.....	0.06	95	0.08	0.25

It will be seen that the emulsion containing a thionamide having a carboxyl substituent is much more effective in preventing the growth of incubation fog than is a thionamide which does not contain an acid substituent.

EXAMPLE 3

Photographic emulsions are prepared by adding stabilizer compounds having the formula



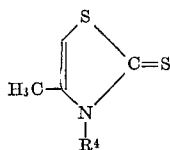
wherein R⁴ and R⁵ are defined in Table 3 to separate portions of a high speed gold and sulfur sensitized bromiodide emulsion containing a spectral sensitizer. Each emulsion sample is coated on a cellulose acetate film support at a coverage of 350 milligrams of silver and 840 milligrams of gelatin per square foot. A sample of each film coating is exposed on an intensity scale sensitometer, processed for five minutes at 68° F. in Kodak Developer DK-50, fixed, washed and dried. The photographic results obtained from these tests are listed in Table 3.

TABLE 3

Stabilizer compound			Fresh		1 week		2 weeks, fog
R ₄	R ₅	g./mole Ag	Relative speed	Fog	Relative speed	Fog	
Control.....			100	0.12	83	0.34	1.12
-CHCO ₂ H	-CO ₂ H	3.0	97	0.10	95	0.13	0.18
CH ₃							
-CH ₂ CH ₂ CO ₂ H	-CH ₂ SO ₂ (CH ₂) ₃ CH ₃	0.3	102	0.11	97	0.17	0.35

EXAMPLE 2

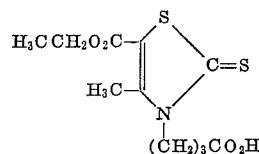
The process of Example 1 is repeated except that the stabilizer compounds added to the emulsions have the formula



wherein R⁴ is defined in Table 2. The emulsions also contain a spectral sensitizer and, in several samples, an additional compound or compounds as indicated in Table 2. Development is accomplished in Kodak Developer DK-

EXAMPLE 4

The process of Example 3 is repeated substituting for the stabilizer compounds therein a thionamide having the formula



In several samples, an additional compound as indicated in Table 4 is included. The photographic results obtained are listed in Table 4.

TABLE 4

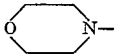
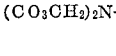
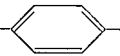
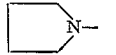
Concentration of stabilizer compound in g./mole Ag	Additional compound and concentration in g./mole Ag	Fresh		1 week incubation at 120° F. and 45% relative humidity	
		Relative speed	Fog	Relative speed	Fog
Control.....		100	0.12	82	0.34
3.0.....		120	0.14	105	0.17
Control.....	Poly(thiodiethylene glutarate) (1.0).	182	0.24		>1.2
3.0.....	do.....	214	0.21	178	0.34
Control.....	Pyridium salt (0.75).....	191	0.21		>1.2
3.0.....	do.....	186	0.19	151	0.33

EXAMPLE 5

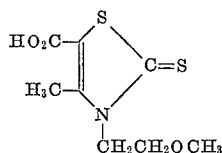
The process of Example 3 is repeated using as the

is also tested for its ability to stabilize an emulsion. The photographic results are set forth in Table 6.

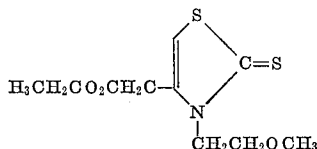
TABLE 6

Dithiocarbamate			Incubation at 120° F. and 50% relative humidity			
$\begin{array}{c} R^3 \\ \\ N- \\ \\ R^4 \end{array}$	R ¹	g./mole Ag	Fresh		1 week	
			Relative Speed	Fog	Relative Speed	Fog
Control.....			100	0.17	62	0.41
	$-CH_2-$ 	0.27	100	0.13	76	0.25
Containing no acid group.....		0.27	29.5	0.22		>1.0
Control.....			100	0.13	57	0.48
	$-CH_2-$ 	3.0	100	0.09	91	0.09
Control.....			100	0.16		0.81
	$-CH(CH_3)(CH_2)_2SO_3^-Na^+$	9.0	107	0.15		0.72

stabilizer a thionamide having the formula



For the purpose of comparison, there is also tested an emulsion containing a non-acid group containing thionamide having the formula



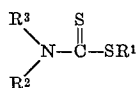
The photographic results obtained are set forth in Table 5.

TABLE 5

		Incubation at 120° F. and 50% relative humidity			
Thionamide	G./mole Ag	Fresh		1 week	
		Relative speed	Fog	Relative speed	Fog
Control.....		100	0.12	59	0.48
Containing acid group.....	0.3	95	0.11	94	0.14
Containing no acid group.....	0.3	78	0.11		>1.0

EXAMPLE 6

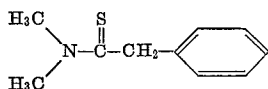
This example illustrates the use of dithiocarbamates containing acid groups as stabilizers for photographic emulsions. The process of Example 2 is repeated using as the stabilizer compound dithiocarbamates having the formula



wherein the groups R¹ and

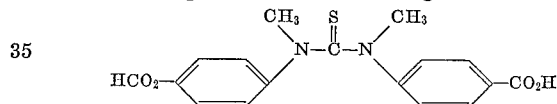


are as defined in Table 6. For purpose of comparison, a non-acid group containing dithiocarbamate having the formula



EXAMPLE 7

This example illustrates the use of a thiourea containing an acid group as a stabilizer for a photographic emulsion. The process of Example 2 is repeated using as the stabilizer compound a thiourea having the formula



The photographic results are set forth below in Table 7.

TABLE 7

Thiourea in g./mole Ag	Fresh		Two weeks' incubation at 120° F. and 50% relative humidity	
	Relative speed	Fog	Relative speed	Fog
Control.....	100	0.14	54	0.35
0.9.....	80	0.11	65	0.14

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In the foregoing Table 4, the pyridinium salt used is 7,18-diazo-6,19 - dioxotetracosane - 1,24-bis(pyridinium perchlorate).

The results in the above tables show that the compounds of this invention prevent the growth of incubation fog when incorporated in photographic emulsions.

Although the invention has been described in considerable detail with reference to certain embodiments thereof, it will be understood that variations and modifications can be effected without departing from the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

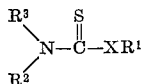
I claim:

1. A composition comprising a silver halide emulsion containing a fog-stabilizing amount of an acyclic or monocyclic thionamide, said thionamide containing at least one carboxylic or sulfonic acid group which will confer a negative charge to the thionamide at a pH of 5 or below.

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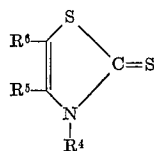
2. The composition of claim 1 wherein said thionamide is present in an amount of about 0.05 gram to about 30.0 grams per mole of silver in said silver halide emulsion.

3. The composition of claim 1 wherein said thionamide has the structure



wherein X is sulfur, oxygen or an iso-electronic group, R¹, R² and R³, when taken separately, are aliphatic groups having up to 10 carbon atoms or substituted aliphatic groups, R¹ and R², when taken together, represent an alkylene group and R² and R³, when taken together with the nitrogen atom to which they are attached, represent a heterocyclic group.

4. The composition of claim 1 wherein said thionamide has the structure



wherein R⁴ is an aliphatic group or a substituted aliphatic group containing up to 10 carbon atoms and R⁵ and R⁶ are hydrogen, aliphatic groups or substituted aliphatic groups containing up to 10 carbon atoms, at least one of said groups containing a carboxylic or sulfonic acid substituent.

5. The composition of claim 3 wherein X in said thionamide is sulfur and at least one of said groups R¹, R² and R³ contains a carboxylic or sulfonic acid substituent.

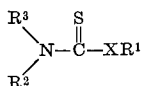
6. The composition of claim 3 wherein X in said thionamide represents the group —NR, R being an aliphatic or substituted aliphatic group having from 1-10 carbon atoms, and at least one of said groups R, R¹, R² and R³ contains a carboxylic or sulfonic acid substituent.

7. A photographic element comprising a support coated with a silver halide layer, said element containing a fog-stabilizing amount of an acyclic or monocyclic thionamide, said thionamide containing at least one carboxylic or sulfonic acid group which will confer a negative charge to the thionamide at a pH of 5 or below.

8. The photographic element of claim 7 wherein said layer is a silver halide emulsion.

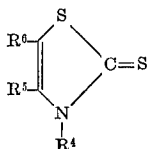
9. The photographic element of claim 8 wherein said thionamide is present in an amount of about 0.05 gram to about 30.0 grams per mole of silver in said silver halide emulsion.

10. The photographic element of claim 8 wherein said thionamide has the structure



wherein X is sulfur, oxygen or an iso-electronic group, R¹, R² and R³, when taken separately, are aliphatic groups having up to 10 carbon atoms or substituted aliphatic groups, R¹ and R², when taken together, represent an alkylene group and R² and R³, when taken together with the nitrogen atom to which they are attached, represent a heterocyclic group.

11. The photographic element of claim 8 wherein said thionamide has the structure



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wherein R⁴ is an aliphatic group or a substituted aliphatic group containing up to 10 carbon atoms and R⁵ and R⁶ are hydrogen, aliphatic groups or substituted aliphatic groups containing up to 10 carbon atoms, at least one of said groups containing a carboxylic or sulfonic acid substituent.

12. The photographic element of claim 10 wherein X in said thionamide is sulfur and at least one of said groups R¹, R² and R³ contains a carboxylic or sulfonic acid substituent.

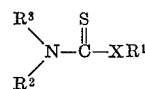
13. The photographic element of claim 10 wherein X in said thionamide represents the group —NR, R being an aliphatic or substituted aliphatic group having up to 10 carbon atoms, and at least one of said groups R, R¹, R² and R³ contains a carboxylic or sulfonic acid substituent.

14. The photographic element of claim 8 wherein said thionamide is present in said silver halide emulsion.

15. The photographic element of claim 8 wherein said thionamide is present in a layer contiguous to said silver halide emulsion.

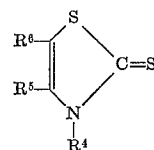
16. In a process of developing a photographic element comprising a support coated with at least one silver halide emulsion layer, the improvement comprising developing said photographic element in the presence of an acyclic or monocyclic thionamide containing at least one carboxylic or sulfonic acid group which will confer a negative charge thereto at a pH of 5 or below.

17. The process of claim 16 wherein said thionamide has the structure



wherein X is sulfur, oxygen or an iso-electronic group, R¹, R² and R³, when taken separately, are aliphatic groups having up to 10 carbon atoms or substituted aliphatic groups, R¹ and R² when taken together, represent an alkylene group and R² and R³, when taken together with the nitrogen atom to which they are attached, represent a heterocyclic group.

18. The process of claim 16 wherein said thionamide has the structure



wherein R⁴ is an aliphatic group or a substituted aliphatic group containing up to 10 carbon atoms and R⁵ and R⁶ are hydrogen, aliphatic groups or substituted aliphatic groups containing up to 10 carbon atoms, at least one of said groups containing a carboxylic or sulfonic acid substituent.

19. The process of claim 17 wherein X in said thionamide is sulfur and at least one of said groups R¹, R² and R³ contains a carboxylic or sulfonic acid substituent.

20. The process of claim 17 wherein X in said thionamide represents the group —NR, R being an aliphatic or substituted aliphatic group having up to 10 carbon atoms, and at least one of said groups R, R¹, R² and R³ contains a carboxylic or sulfonic acid substituent.

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