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3,266,897

ANTIFOGGANT AGENTS FOR PHOTOGRAPHY

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This invention is related to photography, and more particularly to certain mercaptotetrazole compounds, photographic silver halide emulsions containing said compounds, and the development of photographic images in photographic silver halide emulsions in the presence of said compounds.

The photographic development of a light-image-exposed silver halide emulsion layer of a normal photographic film, plate or paper produces in addition to the silver image, a general deposit of metallic silver, the distribution and density of which bears no direct relation to the variations in the light image. This over-all deposit of silver is referred to as fog, i.e., "chemical fog" or "development fog." The fog density adds to the image density and in areas of the image that result from the least exposure, the image contrast is reduced. Usually the fog density produced upon development is higher in high speed emulsions than in the slower emulsions. In general, the more vigorous the development, i.e., the higher the development temperature and/or the stronger the developing agent the more fog is developed in a given emulsion.

The degree to which a photographic emulsion layer produces fog upon development usually increases with the age of the emulsion particularly when the material has been stored under warm and humid conditions.

It is known to incorporate 1-phenyl-5-mercaptotetrazole in photographic silver halide emulsion layers as an antifoggant. In many instances, however, the use of this compound has resulted in considerable desensitization. Other antifoggants are desired that do not tend to desensitize the emulsion that they are incorporated in.

It is an object of our invention to provide antifoggants that can be incorporated in silver halide emulsions at much higher concentrations than prior art antifoggants, resulting in good suppression of fresh and incubation fog with little of the speed loss (especially on incubation) associated with prior art antifoggants.

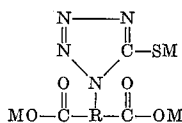
Another object is to provide photographic silver halide emulsion layers containing our antifoggant.

Another object is to provide a process for developing a silver image from a latent image in a silver halide emulsion layer by contacting the layer with an aqueous alkaline solution of a silver halide developing agent in the presence of one of our antifoggants.

Still other objects will become evident from a consideration of the following specification and claims.

These and other objects are accomplished according to our invention by the use of antifoggant agents having the formula:

(I)

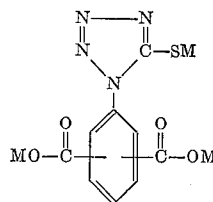


wherein R represents a hydrocarbon group, such as, an aryl group, e.g., phenyl, naphthyl, etc., an alkyl group, e.g., methyl, ethyl, propyl, butyl, hexyl, benzyl, ethylphenyl, etc.; and M represents a group, such as, the hydrogen atom, an alkali metal (e.g., sodium atom, potassium atom, lithium atom, etc.), the NH_4 — group, etc.

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Preferred compounds of our invention include those represented by the formula:

(II)

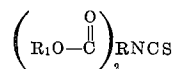


wherein M is as defined previously.

Our antifoggant agents are preferably incorporated in the silver halide emulsion during its manufacture or incorporated in the silver halide developer solution, however, any other method may be used to bring our antifoggant agent into operative contact with the emulsion, for example, the compound can be incorporated in a subcoat, supercoat or backing layer which is in contact with or comes in contact with the emulsion layer.

In general our antifoggant agents are produced advantageously by reacting a compound having the formula:

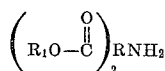
(III)



wherein R is as defined previously and R_1 represents an alkyl group, e.g., methyl, ethyl, etc., with an alkali metal azide such as sodium azide in a suitable solvent, preferably by heating between room temperature and the reflux temperature of the reaction mixture. The R_1 group is replaced by an M group after the tetrazole ring is formed by the reaction.

Compounds of Formula III are formed advantageously by reacting thiophosgene in water with a compound of the formula:

(IV)



wherein R_1 and R are as defined previously.

The following typical examples will serve to illustrate but not limit our invention.

Example 1.—1-(3,5-dicarboxyphenyl)-5-mercaptotetrazole

A suspension of 100 g. (0.87 mol.) of thiophosgene in 250 ml. of water was mixed thoroughly and treated in one portion with 121 g. (0.58 mol.) of dimethyl-5-aminoisophthalate. The mixture was stirred rapidly and efficiently for 1½ hours. The precipitated solid was collected, washed thoroughly with water, and air dried overnight in a hood. The solid was recrystallized from cyclohexane to give 115 g. of 3,5-dicarboxyphenylisothiocyanate, M.P. 114°–115° C.

A mixture of 25.1 g. (0.1 mol.) of the isothiocyanate and 20 g. (0.3 mol.) of sodium azide in 1500 ml. of water was stirred and refluxed for 2–4 hours. The mixture was filtered hot; the filtrate cooled and acidified with dilute hydrochloric acid. The precipitated solid was collected, washed thoroughly with water and pulled dry. The solid was transferred to a flask with excess sodium hydroxide solution and heated on a steam bath for one hour. The solution was cooled and acidified with dilute hydrochloric acid. The white solid was collected, washed with water, pulled dry and recrystallized from methanol-water. The 2–3 g. of product obtained had a M.P. of 218° C. with decomposition.

Calculated for $\text{C}_9\text{H}_5\text{N}_4\text{O}_4\text{S}$: C, 40.6; H, 2.3; N, 21.0; S, 12.1. Found: C, 39.8; H, 2.4; N, 21.2; S, 11.8.

Example 2.—1-(2,5-dicarboxyphenyl)-5-mercaptotetrazole

This compound was prepared by the method used to make Compound No. 1 but substituting an equivalent amount of 5-amino-dimethyl-1,4-benzene dicarboxylate for the dimethyl-5-aminoisophthalate. The recrystallized product was pale yellow and had a M.P. of 200° C. with decomposition when heated rapidly, however did not melt up to 300° C. when heated slowly.

Example 3.—1-(3,5-dicarboxyphenyl)-5-mercaptotetrazole (disodium salt)

This compound may be prepared from Compound No. 1 by treating a methanolic solution with 2 equivalents by sodium hydroxide and separating the sodium salt that precipitated.

Example 4.—1-(2,5-dicarboxyphenyl)-5-mercaptotetrazole (trisodium salt)

This compound may be prepared from Compound No. 2 by treating a methanolic solution with 3 equivalents of sodium hydroxide and separating the sodium salt that precipitated.

Similarly, still other compounds of Formula I are prepared for use according to our invention, for example, compounds such as 1-(2,3-dicarboxyphenyl)-5-mercaptotetrazole, 1-(3,4-dicarboxyphenyl)-5-mercaptotetrazole, 1-(3,5-dicarboxybenzyl)-5-mercaptotetrazole, 1-(2-propanedioic acid)-5-mercaptotetrazole.

Our compounds of Formula I are used to advantage in making silver halide emulsions. Our emulsions contain silver halide grains such as silver chloride, silver bromide, silver iodide, silver chlorobromide, silver bromiodide, silver chlorobromiodide, etc., dispersed in a hydrophilic colloid, such as, natural materials, e.g., gelatin, albumin, agar-agar, gum arabic, alginic acid, etc., and any of the synthetic hydrophilic resins that are substituted for gelatin, e.g., polyvinyl alcohol, polyvinyl pyrrolidone, cellulose ethers, partially hydrolyzed cellulose acetate, etc.

The antifogging agents of our invention are added advantageously to the silver halide emulsion as a solution in a suitable solvent, e.g., water, methanol, ethanol, etc. Our compounds can be added to the silver halide emulsion at any time during its preparation; however, it is preferred to add it to the finished emulsion with intimate mixing as the final addenda before coating. The compounds can be used advantageously over a wide range of concentrations, for example, an operative range is from about 0.1 g. to about 10 g. per mole of silver halide, with a preferred range of from about 0.25 g. to about 2 g. per mole of silver halide. The optimum amount of the antifogging agent to be used will depend upon the particular emulsion, the developer solution, etc., and the particular results desired. The optimum amount of our compound to be added can be determined for a given emulsion by methods well known in the art.

Our photographic silver halide emulsions may also contain such addenda as chemical sensitizers, e.g., sulfur sensitizers (e.g., allyl thiocarbamide, thiourea, allylthiocyanate, cystine, etc.), various gold compounds (e.g., potassium chloraurate, auric trichloride, etc.) (see U.S. patents to W. D. Baldisiefen 2,540,085, granted February 6, 1951; R. E. Damschroder 2,597,856, granted May 27, 1952, and H. C. Yutzy et al. 2,597,915, granted May 27, 1952), various palladium compounds, such as palladium chloride (W. D. Baldisiefen U.S. 2,540,086, granted February 6, 1951), potassium chloro-palladate (R. E. Stauffer et al. U.S. 2,588,079, granted May 27, 1952), etc., or mixture of such sensitizers; optical sensitizers, such as those described in Brooker U.S. Patents 1,846,301, issued February 23, 1932; 1,846,302, issued February 23, 1932; and 1,942,854, issued January 9, 1934; White U.S. Patent 1,990,507, issued February 12, 1935; Brooker and White U.S. Patents 2,112,140, issued March 22, 1938; 2,165,338,

issued July 11, 1939; 2,493,747, issued January 10, 1950, and 2,739,964, issued March 27, 1956; Brooker and Keyes U.S. Patent 2,493,748, issued January 10, 1950; Sprague U.S. Patents 2,503,776, issued April 11, 1950, and 2,519,001, issued August 15, 1950; Heseltine and Brooker U.S. Patent 2,666,761, issued January 19, 1954; Heseltine U.S. Patent 2,734,900, issued February 14, 1956; Van Lare U.S. Patent 2,739,149, issued March 20, 1956; and Kodak Limited British Patent 450,958, accepted July 15, 1936; hardeners, such as formaldehyde (A. Miller, U.S. 1,763,533, granted June 10, 1930), chrome alum (U.S. 1,763,533), glyoxal (J. Brunken U.S. 1,870,354, granted August 9, 1932), dibromacrolein (O. Block et al. British 406,750, accepted March 8, 1934), etc.; color couplers, such as those described in I. R. Salminen et al. U.S. Patent 2,423,730, granted July 7, 1947, Spence and Carroll U.S. Patent 2,640,776, issued June 2, 1953, etc.; or mixtures of such addenda. Dispensing agents for color couplers, such as those set forth in U.S. patents to E. E. Jelley et al. 2,322,027, granted June 15, 1943, and L. D. Mannes et al. 2,304,940, granted December 15, 1942, can also be employed in the above-described emulsions.

Our emulsions are coated to advantage on any of the materials used for photographic elements including, for example, paper, glass, cellulose acetate, cellulose nitrate, synthetic film-forming resins, etc.

The following examples will serve to further illustrate our invention.

Example I

A coarse grain gelatino silver bromiodide emulsion that was chemically sensitized with sulfur and gold compounds and spectrally sensitized with cyanine dyes was divided into three portions. One portion was used as a control. The other portions were treated with the indicated amount of antifogant. Coatings were made of each emulsion on a cellulose acetate film base, chill set and dried. Film samples were exposed on an Eastman IB Sensitometer for 1/25 second to light of daylight quality and were developed for five minutes in a developer having the composition:

	G.
p-Methylaminophenol sulfate	2.5
Sodium sulfite, desiccated	30.0
Hydroquinone	2.5
Sodium metaborate octahydrate	10.0
Potassium bromide	0.5
Water to make, 1.0 l.	

at 68° F., fixed in a conventional sodium thiosulfate fixing bath, washed and dried. The spread was determined from the exposure necessary to produce a density of 0.2 above fog. The data for fresh coatings and for incubated coatings are summarized in the following table.

TABLE I

Addendum		Fresh Emulsion Coating			Emulsion Coating Incubated for 2 Weeks at 120° F.		
		Relative Speed	γ	Fog	Relative Speed	γ	Fog
Compound	g./mole of AgX						
Control.....	0	100	1.17	.13	22	0.62	.97
No. 1.....	0.9	95	1.18	.07	94	1.08	.15
A.....	0.06	54	0.95	.07	63	1.08	.12

Compound A is 1-phenyl-5-mercaptotetrazole.

The results show that our Compound No. 1 can be used to substantially reduce the fog level in an emulsion without appreciably reducing its relative speed, while an emulsion treated with 1-phenyl-5-mercaptotetrazole to reduce the fog to the same level had a 46% loss in relative speed. Incubation of our emulsion coating for two weeks at 120° F. produced no appreciable loss in speed

and relatively little increase in fog level compared with the control.

Example II

A high-speed negative pan-sensitized gelatino-silver bromiodide emulsion was divided into portions to which the indicated amounts of antifoggant agents were added. Coatings of each emulsion were made, exposed and processed as described in Example I. The results are summarized in the following table.

TABLE 2

Addendum		Fresh Emulsion Coating			Emulsion Coating Incubated for 2 Weeks at 120° F.		
Compound	g./mole of AgX	Relative Speed	γ	Fog	Relative Speed	γ	Fog
Control-----	0	100	1.17	.13	22	.62	.97
A-----	.03	85	1.13	.08	80	1.02	.20
A-----	.06	54	0.95	.07	63	1.08	.12
Control-----	0	100	1.30	.11	33	.75	.84
1-----	.9	97	1.30	.07	100	1.22	.13
1-----	1.8	94	1.30	.07	97	1.22	.09
2-----	.9	87	1.33	.08	102	1.13	.12
Control-----	0	100	1.12	.10	-----	-----	-----
B-----	.037	36	1.37	.06	-----	-----	-----

Compound A is 1-phenyl-5-mercaptotetrazole.

Compound B is 1-(3-carboxyphenyl)-5-mercaptotetrazole.

From the data it can be seen that Compounds 1 and 2 can be used advantageously at much higher concentrations in silver halide emulsions than Compound A, 1-phenyl-5-mercaptotetrazole, resulting in good suppression of fresh and incubation fog with little of the speed loss (especially on incubation) associated with the parent Compound A. Compound B, 1-(3-carboxyphenyl)-5-mercaptotetrazole desensitized the emulsion very strongly.

The valuable desensitizing characteristics exhibited by our Compounds 1 and 2 are very unexpected from the characteristics exhibited by Compounds A and B when used in the same silver halide emulsion and under the same conditions.

Similarly, it can be shown that other compounds of Formula I can be used to advantage in silver halide emulsions to produce substantial reductions in fog with relatively little loss in speed in both fresh as well as incubated emulsion coatings.

The following example will serve to illustrate the use of our compounds of Formula I in developer solutions according to our invention.

Example III

A high speed silver bromiodide emulsion coated on a support at 300 mg. of silver/ft.² and 500 mg. of gelatin/ft.² was exposed through a 0.6 neutral density filter in an Eastman 1B sensitometer having an intensity scale with 0.15 neutral density increments for $\frac{1}{50}$ of a second to light of 3000° K. from a 500 w. electric lamp. One piece of the exposed film was given 16 minutes development in a color developer at 70° F. with nitrogen burst agitation, the developer having the composition:

Sodium hexameta phosphate -----	G.
Sodium sulfite, anhydrous -----	2
2-amino-5-diethylaminotoluene monohydrochloride --	4
Sodium carbonate·H ₂ O -----	3
Potassium bromide -----	20
1-amino-8-naphthol-3,6-disulfonic acid, disodium salt -----	2
Water to 1 l.	5

pH 10.65.

The developed film was treated for 30 seconds in a conventional stop bath, fixed for 5 minutes in a conventional sodium thiosulfate fix bath, washed for 10 minutes and

dried. Density measurements made on the processed film showed the fog was .18 and D max. was 1.20.

A second piece of the exposed film was given the same process except that the color developer solution contained 149 mg. of 1-(3,5-dicarboxyphenyl)-5-mercaptotetrazole per liter. Density measurements showed that the fog was 10% lower than the control and the D max. was 1.20.

Similarly, it can be shown that other compounds of Formula I can be used to advantage in developer solutions, and that photographic emulsions developed in these developer solutions have substantially lower fog levels with no loss in D max. as compared to the same films developed in the same developer solution containing none of our mercaptotetrazole compounds. Our developers contain from 1-500, preferably from 100-200 mg./l., of our antifoggants.

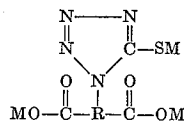
Our compounds of Formula I are used to advantage in any of the photographic silver halide developer compositions comprising water, an alkali, and a silver halide developing agent. Alkali material useful in our developers include, sodium carbonate, potassium carbonate, trisodium phosphate, sodium pyroborate, sodium metaborate, sodium hydroxide, potassium hydroxide, etc. Silver halide developing agents used to advantage include, a hydroquinone, e.g., hydroquinone substituted on the 2, 3, 5, or 6 carbons or any combination of these with lower alkyl groups such as methyl, ethyl, propyl, butyl, etc., with alkoxy groups, halogen atoms, such as chlorine, bromine, etc., and with other groups commonly used as substituents; resorcinol; catechol; ascorbic acid, gallic acid; a 1-phenyl-3-pyrazolidone, such as are described in Hood et al. U.S. 2,751,297, issued June 19, 1956, e.g., 1-phenyl-3-pyrazolidone, 1-phenyl-5-methyl-3-pyrazolidone, 1-phenyl-4,4-dimethyl-3-pyrazolidone, etc.; an aminophenol, e.g., p-methylaminophenol sulfate, etc.; a phenylenediamine, e.g., N,N-diethyl-p-phenylenediamine hydrochloride, N-methyl-p-phenylenediamine hydrochloride, N,N-dimethyl-p-phenylenediamine hydrochloride, 2-amino-5-N,N-diethylaminotoluene hydrochloride, 2-amino-5-(N-ethyl-N-lauryl)toluene, N-ethyl- β -methanesulfonamidoethyl-3-methyl-4-aminoaniline sulfate, N-ethyl- β -methanesulfonamidoethyl-4-aminoaniline, 4-N-ethyl-N- β -hydroxyethylaminoaniline, etc.; or combinations of the above developing agents. Our developer compositions may contain any of the addenda conventionally used, including preservatives such as alkali metal sulfites, e.g., sodium sulfite, potassium sulfite, etc., an alkali metal bisulfite, e.g., sodium bisulfite, etc., an alkali metal metabisulfite, e.g., potassium metabisulfite, etc., alkali metal bromides, e.g., sodium bromide, potassium bromide, etc., etc.

The antifoggants of our invention are also used to advantage in black-and-white image transfer systems of the type described in patents, such as, Rott U.S. 2,352,014, issued June 20, 1944; Land U.S. 2,543,181, issued February 7, 1951, etc., as well as in color image transfer systems of the type described in patents such as Yutzy U.S. 2,756,141, issued July 14, 1956; Whitmore French 1,293,709; Weyerts French 1,313,767; Rogers U.S. 2,983,606; issued May 9, 1961; etc.

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

We claim:

1. A light-sensitive photographic emulsion comprising silver halide grains and a compound having the formula:



wherein R represents a hydrocarbon and M represents a member selected from the class consisting of the hydrogen atom, an alkali metal atom, and the NH_4 — group.

2. A light-sensitive photographic emulsion comprising silver halide grains and a 1-(dicarboxyphenyl)-5-mercaptotetrazole.

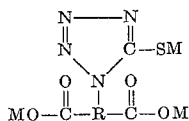
3. A light-sensitive photographic emulsion of claim 1 in which the silver halide grains are chemically sensitized.

4. A light-sensitive photographic emulsion of claim 1 in which the silver halide grains are chemically sensitized with sulfur and gold, and spectrally sensitized with a cyanine dye.

5. A light-sensitive photographic emulsion comprising silver halide grains and 1-(3,5-dicarboxyphenyl)-5-mercaptotetrazole.

6. A light-sensitive photographic emulsion comprising silver halide grains and 1-(2,5-dicarboxyphenyl)-5-mercaptotetrazole.

7. A light-sensitive photographic element comprising a support coated with at least one light-sensitive layer comprising a hydrophilic colloid, silver halide grains and a mercaptotetrazole compound having the formula:



wherein R represents a hydrocarbon and M represents a member selected from the class consisting of the hydrogen atom, an alkali metal atom, and the NH_4 — group.

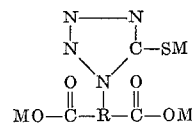
8. A light-sensitive photographic element comprising a support coated with at least one light-sensitive layer comprising a hydrophilic colloid, silver halide grains and a 1-(dicarboxyphenyl)-5-mercaptotetrazole.

9. A light-sensitive photographic element comprising a support coated with at least one light-sensitive layer comprising a hydrophilic colloid, silver halide grains and 1-(3,5-dicarboxyphenyl)-5-mercaptotetrazole.

10. A light-sensitive photographic element comprising a support coated with at least one light-sensitive layer comprising a hydrophilic colloid, silver halide grains and 1-(2,5-dicarboxyphenyl)-5-mercaptotetrazole.

11. A process for forming a visible silver image from a latent image in a light-sensitive photographic silver halide emulsion layer comprising the step of contacting

the said emulsion layer with an aqueous alkaline solution of a silver halide developing agent in the presence of a substituted mercaptotetrazole compound having the formula:



wherein R represents a hydrocarbon and M represents a member selected from the class consisting of the hydrogen atom, an alkali metal atom, and the NH_4 — group.

12. A process of claim 11 in which the mercaptotetrazole compound is a 1-(dicarboxyphenyl)-5-mercaptotetrazole.

13. A process of claim 11 in which the mercaptotetrazole is 1-(3,5-dicarboxyphenyl)-5-mercaptotetrazole.

14. A process of claim 11 in which the mercaptotetrazole is 1-(2,5-dicarboxyphenyl)-5-mercaptotetrazole.

15. A photographic developer composition comprising water, an alkali, a silver halide developing agent and a compound having the formula:



wherein R represents a hydrocarbon and M represents a member selected from the class consisting of the hydrogen atom, an alkali metal atom, and the NH_4 — group.

16. A photographic developer composition comprising water, an alkali, a silver halide developing agent, and a 1-(dicarboxyphenyl)-5-mercaptotetrazole.

17. A photographic developer composition comprising water, an alkali, a silver halide developing agent and 1-(3,5-dicarboxyphenyl)-5-mercaptotetrazole.

18. A photographic developer composition comprising water, an alkali, a silver halide developing agent and 1-(2,5-dicarboxyphenyl)-5-mercaptotetrazole.

No references cited.

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