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3,598,602

s-TRIAZOLO[4,3-b]-s-TRIAZOLES AND DERIVATIVES AS ANTIFOGGANTS FOR PHOTOGRAPHIC EMULSIONS

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14 Claims

ABSTRACT OF THE DISCLOSURE

7H-s-triazolo[4,3-b]-s-triazole and 5H-s-triazolo-[4,3-b]-s-triazole and their derivatives are used with photographic silver halide elements in emulsions in order to stabilize said elements and emulsions against fog.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to photography. In one aspect, this invention relates to the stabilization of photographic silver halide elements and emulsions against spontaneous fog without adversely affecting the photographic sensitivity of said silver halide elements and emulsions.

Description of the prior art

It is well known that photographic silver halide on storage tends to lose sensitivity and to become spontaneously developable without exposure to light. The detectable amount of silver salt reduced during development of those areas where there is no exposure is commonly referred to as fog, and more specifically "chemical fog" where it is desirable to distinguish between it and the effects of accidental exposure to radiation.

Fog depends upon both the particular emulsion and the conditions of development. For a given emulsion fog increases with the degree of development. At constant development conditions fog generally increases with the temperature, time and relative humidity of storage conditions.

It is known that certain mercaptans, particularly those compounds having mercapto substitution on a heterocyclic ring, and certain organic disulfides have an antifoggant and stabilizing effect when incorporated in photographic silver halide emulsions. For example, U.S. Pat. 2,440,110 discloses organic disulfides used in combination with sulfenic or seleninic acids or their salts, U.S. Pat. 2,819,965 describes the use of s-triazines having a carboxymethyl-mercapto substituent, U.S. Pat. 2,935,404 described bis-(s-triazolo[4,3-a]pyrimidine) disulfides, British 819,370 describes mercapto-1,2,4-triazines. Many of the prior art compounds are objectionable either because they are not effective antifoggants unless used in combination with other materials, while other compounds have a desensitizing effect at concentrations wherein said compounds are most effective as antifoggants. It is therefore desirable to obtain compounds which are effective antifoggants for photographic silver halide elements and emulsions without effecting a desensitization of said elements and emulsions.

SUMMARY OF THE INVENTION

In accordance with this invention, it has been found that significantly enhanced stability against chemical fog in a photographic silver halide layer can be obtained while not seriously effecting a decrease in the photographic sensitivity of said layer. The enhanced stability and control over chemical fog is obtained through the use of compounds not known, heretofore, to have antifoggant properties.

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It is the object, according to one aspect of this invention, to provide stabilized photographic silver halide emulsions and layers.

It is another aspect of this invention to provide a method for stabilizing silver halide layers.

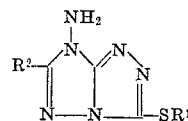
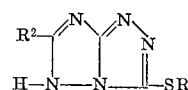
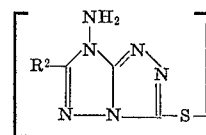
It is yet a further object to stabilize silver halide layers without adversely affecting, to any substantial degree, the photographic sensitivity of said layers.

It is a further object of this invention to provide photographic silver halide layers which are stabilized with a particular group of triazoles.

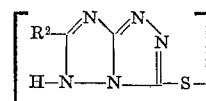
Other objects will become apparent from examination and consideration of the specification and claims.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

It has been found that certain triazoles act as strong antifoggants and stabilize photographic silver halide layers without causing a serious reduction in the sensitivity of said layers. The triazoles which have been found useful have the following formulas:



and



Wherein each R¹ is H, alkyl, aryl, or hydroxyalkyl and each R² is H, alkyl, aryl, halogen, alkoxy or hydroxy. R¹ or R² radicals include those containing 1 to 20 carbon atoms or more and preferably 1 to 10 carbon atoms. Suitable radicals are often hydrocarbyl but non-hydrocarbyl radicals can also be used.

Typical R¹ radicals are methyl, ethyl, propyl, decyl, phenyl, tolyl, hydroxyethyl, hydroxypropyl and the like. Typical R² radicals are methyl, ethyl, propyl, decyl, phenyl, tolyl, methoxy, butoxy and the like.

Examples of the triazole derivatives are:

7-amino-6-methyl-7H-s-triazolo[4,3-b]-s-triazole-3-thiol;
7-amino-7H-s-triazolo[4,3-b]-2-triazole-3-thiol;
5H-s-triazolo[4,3-b]-s-triazole-3-thiol;
7-amino-3-methylthio-7H-s-triazolo[4,3-b]-s-triazole;
bis(6-methyl-5H-s-triazolo[4,3-b]-s-triazol-3-yl) disulfide;
bis(5H-s-triazolo[4,3-b]-s-triazol-3-yl) disulfide;
and the like.

The compounds found to be useful in this invention are conveniently prepared by the methods disclosed in "Chemistry and Industry" (1966), p. 2168, and in "Journal of Organic Chemistry," 33 (1968), p. 143.

The concentration of the stabilizing compounds can vary considerably depending on various factors such as: the effects desired, silver content of the photographic layer, the nature of the particular silver halide layer, the degree of ripening, the location of the stabilizer in relation to the silver halide layer, the particular stabilizer, etc. In

general, a concentration in the range of about 0.001 gram to about 10 grams of stabilizer per mole of silver halide is useful. A preferred range is from about 0.01 gram to about 1 gram of stabilizer per mole of silver halide. In accordance with the invention one may use the higher concentrations without inducing a reduction in photographic sensitivity. The optimum concentration of stabilizer can be determined through techniques well-known in the art.

The stabilizing addenda can be added in a variety of ways and at various stages in the preparation of the photographic system. The stabilizers can be incorporated directly into silver halide elements and emulsions, preferably before the final digestion operation in the case of emulsions and after the silver halide grains are substantially in their final size and shape. The addenda can be added to a layer adjacent to the silver halide layer. The solvents in which the stabilizers may be dissolved are restricted to those that are not harmful to the silver halide layer and in accordance with the general practice organic solvents and diluents are preferred.

The light-sensitive silver halide emulsion of a photographic element comprising the antifoggants of this invention can contain addenda such as gelatin plasticizers, coating aids and hardeners such as the aldehyde-type hardeners, e.g., formaldehyde, mucochloric acid, glutaraldehyde bis(sodium bisulfite), maleic dialdehyde, and aziridines, dioxane derivatives, vinylsulfonylethers and oxypolysaccharides. 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. Spectral sensitizers which can be used are the cyanines, merocyanines, complex (trinuclear) cyanines, complex (trinuclear) merocyanines, styryls and heimcyanines. Developing agents can also be incorporated into the emulsion if desired or can be contained in a separate underlayer.

The stabilizing addenda employed in the practice of this invention can be used in various kinds of photographic emulsions. In addition to be useful in orthochromatic, panchromatic and infrared emulsions, they are also useful in X-ray and other non-spectrally sensitized emulsions. They can be added to the emulsions before, simultaneously, or after any spectrally sensitizing dyes that may be used. They are particularly effective in sulfur and gold sensitized silver halide emulsions. Various silver salts can be used as sensitive salts, including, for example, silver bromide, silver iodide, silver chloride, silver chlorobromide, silver bromiodide or silver chloriodide and the like. The silver halides 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 subject addenda 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. 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.

In the preparation of the silver halide dispersions employed for preparing silver halide emulsions there can be employed as the dispersing agent, or "binders" as they are known in the art, for the silver halide in its preparation, gelatin or some other colloidal material such as modified gelatin, colloidal albumin, a cellulose derivative, polyvinyl compound, acrylamine polymers, etc., although gelatin is preferred. 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 Yudelsohn issued Nov. 6, 1962; and 3,220,844 of Houck, Smith and Yudelsohn 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 photographic emulsion stabilized according to this invention can be coated on a wide variety of supports. Typical supports include those generally employed for photographic elements, as exemplified by cellulose nitrate film, cellulose ester film, poly(vinyl acetal) film, polystyrene film, poly(ethylene terephthalate) film and related films of resinous materials as well as glass, paper, metal, wood and the like. Supports such as paper that are coated with alpha-olefin polymers, particularly polymers of alpha-olefins containing two or more carbon atoms, as for example, polyethylene, polypropylene, ethylene-butene copolymers and the like, can also be employed.

Photographic layers comprising the antifoggants 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 layer.

Silver halide emulsions containing the antifoggants of 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 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. Pats. 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.

The following examples are included for a further understanding of the invention:

EXAMPLE 1

The compound 7-amino-7H-s-triazolo[4,3-b]-s-triazole-3-thiol is incorporated into a high speed gelatin photographic silver bromiodide emulsion. The emulsion is coated on a cellulose acetate film support at a coverage of 459 mg. of silver and 1040 mg. of gelatin per square foot and cut into strips. As a control, a similar emulsion is prepared without a stabilizer and coated on cellulose acetate film support and cut into strips in the same manner. Sample strips of each of the prepared coatings are exposed in an intensity scale sensitometer (Kodak Type 1B), processed for 5 minutes in Kodak DK-50 developer, fixed, washed and dried. A second group of the prepared photographic emulsions are incubated for 2 weeks at 120° F. and 50% relative humidity; upon completion of the incubation period the films are exposed and developed in the same manner as the freshly prepared samples. The results of the sensitometric tests on the fresh and incubated samples are summarized in Table I below.

EXAMPLE II

Samples of film strips are prepared as in Example I utilizing other triazoles of this invention. The film strips

are exposed and processed as in Example I. The results are summarized in Table II below.

stabilizer is present at a concentration of from about 0.001 to about 10 grams per mole of silver halide.

TABLE I

Stabilizing compound (g./mole of Ag)	Fresh test			2 weeks incubation at 120° F., 50% relative humidity		
	Relative speed	Gamma	Fog	Relative speed	Gamma	Fog
None (control)-----	100	1.42	.18	54	1.05	.54
.009 ¹ -----	80	1.47	.13	78	1.23	.18

¹ 7-amino-7H-s-triazolo[4,3-b]-s-triazole-3-thiol.

TABLE II

Stabilizing compound (g./mole of Ag)	Fresh test			2 weeks incubation at 120° F., 50% relative humidity		
	Relative speed	Gamma	Fog	Relative speed	Gamma	Fog
None (control)-----	100	1.48	.16	35	.92	.73
0.03 ¹ -----	69	1.35	.10	58	1.10	.14
.09 ² -----	43	1.40	.10	29	1.23	.21
.009 ³ -----	83	1.52	.14	67	1.17	.23
.009 ⁴ -----	78	1.52	.14	62	1.27	.19
.9 ⁵ -----	112	1.60	.15	57	1.10	.40

¹ 7-amino-6-methyl-7H-s-triazolo (4,3-b)-s-triazole-3-thiol.

² 5H-s-triazolo[4,3-b]-s-triazole-3-thiol.

³ Bis(6-methyl-5H-s-triazolo[4,3-b]-s-triazol-3-yl)disulfide.

⁴ Bis (5H-s-triazolo[4,3-b]-s-triazol-3-yl)disulfide.

⁵ 7-amino-3-methylthio-7H-s-triazolo[4,3-b]-s-triazole.

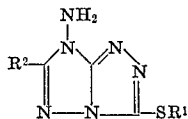
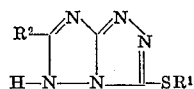
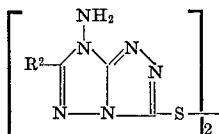
From a study of Tables I and II it can be readily noted that the compounds of this invention are highly useful as stabilizers against fog with respect to silver halide layers.

The invention, it is seen, provides photographic silver halide layers stabilized with the particular antifoggants, said antifoggants not causing any substantial deleterious effect upon speed or photographic sensitivity.

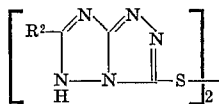
The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

I claim:

1. A photographic element comprising a support, a silver halide layer and a stabilizing compound having a formula selected from the group consisting of:



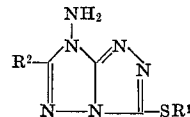
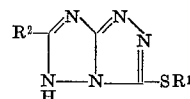
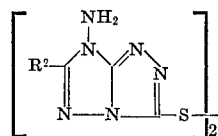
and



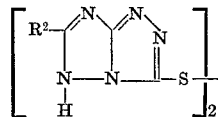
wherein each R¹ is H, alkyl, aryl or hydroxyalkyl, each R² is H, alkyl, aryl, halogen, alkoxy or hydroxy.

2. A photographic element as in claim 1 wherein said

3. A photographic silver halide emulsion comprising a stabilizing compound having a formula selected from the group consisting of:



and



wherein each R¹ is H, alkyl, aryl or hydroxyalkyl, each R² is H, alkyl, aryl, halogen, alkoxy or hydroxy.

4. A photographic emulsion as in claim 3 wherein said stabilizer is present at a concentration of from about 0.01 to about 1 gram per mole of silver halide.

5. A photographic emulsion as in claim 3 wherein R¹ and R² are radicals containing up to 20 carbon atoms.

6. A photographic emulsion as in claim 3 wherein R¹ and R² contain from 1 to 10 carbon atoms.

7. A photographic emulsion as in claim 3 wherein said stabilizer is 7-amino-6-methyl-7H-s-triazolo[4,3-b]-s-triazole-3-thiol.

8. A photographic emulsion as in claim 3 wherein said stabilizer is 7-amino-7H-s-triazolo[4,3-b]-s-triazole-3-thiol.

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9. A photographic emulsion as in claim 3 wherein said stabilizer is 5H-s-triazolo[4,3-b]-s-triazole-3-thiol.

10. A photographic emulsion as in claim 3 wherein said stabilizer is bis(6-methyl-5H-s-triazolo[4,3-b]-s-triazole-3-yl)disulfide.

11. A photographic emulsion as in claim 3 wherein said stabilizer is 7-amino-methylthio-7H-s-triazolo[4,3-b]-s-triazole.

12. A photographic emulsion as in claim 3 wherein said stabilizer is bis(5H - s - triazolo[4,3-b]triazol-yl)disulfide.

13. A photographic silver halide emulsion as in claim 3 wherein said silver halide emulsion is a high-speed gelatino silver bromiodide emulsion.

14. A method for stabilizing photographic silver halide against fog which comprises contacting said silver halide

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with a stabilizing compound having a formula according to claim 1.

References Cited

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