United States Patent

[11] 3,630,745

[72] Inventors **Dorothy J. Beavers; Norman W. Kalenda, both of Rochester, N.Y.**

[21] Appl. No. **864,887**
[22] Filed **Oct. 8, 1969**
[45] Patented **Dec. 28, 1971**

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

---

[54] THIAZOLO [5,4-C]ISOQUINOLINE AND THIAZOLO [4,5-C]IOSQUINOLINE AND DERIVATIVES AS ANTIFOGGANTS FOR PHOTOGRAPHIC LAYERS

11 Claims, No Drawings

[52] **U.S. Cl.** **96/109,** 96/66.5, 260/155, 260/302

[51] **Int. Cl.** **C07d 35/34,** C07d 91/42, G03c 1/34

[50] **Field of Search** 96/109, 66.4, 67, 66.5; 260/155, 157, 158, 298, 302

[56] **References Cited**

UNITED STATES PATENTS

2,948,615	8/1960	Dersch	96/109
3,046,130	7/1962	Dersch	96/109 X
3,084,044	4/1963	Dersch	96/109 X
3,271,154	9/1966	Dersch	96/109 X
3,418,131	12/1968	Bigelow	96/109

Primary Examiner—John T. Goolkasian
Assistant Examiner—M. E. McCamish
Attorneys—William H. J. Kline, Bernard D. Wiese and Allen P. Rosenberg

---

ABSTRACT: Thiazolo [5,4-c]isoquinoline and thiazolo [4,5-c]isoquinoline and their derivatives are used in silver halide elements and emulsions in order to stabilize said elements and emulsions against fog.

THIAZOLO [5,4-C]ISOQUINOLINE AND THIAZOLO [4,5-C]IOSQUINOLINE AND DERIVATIVES AS ANTIFOGGANTS FOR PHOTOGRAPHIC LAYERS

BACKGROUND OF THE INVENTION

1. 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 emulsion.

2. 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. No. 2,440,110 discloses organic disulfides used in combination with sulfinic or seleninic acids or their salts, U.S. Pat. No. 2,819,965 describes the use of s-triazines having a carboxymethylmercapto substituent U.S. Pat. No. 2,935,404 describes bis-(s-triazolo[4,3-a] pyrimidine) disulfides, British Pat. No. 819,370 describes mercapto-1,2,4-triazines.

Quinolines have been used as emulsion addenda. P. Glafkides, Photographic Chemistry, (1958) Vol. 1, page 376 describes 2-aminothiazole-5',4',5,6-quinoline as a stabilizer for neutral and ammoniacal emulsions. Isoquinolines have been used as emulsion addenda, for example, U.S. Pat. No. 2,512,721 describes 3-methylisoquinoline as toners. The inventor is not aware of a disclosure showing the isoquinolines employed in this invention being used as photographic antifoggants.

Many of the prior art stabilizers are objectionable 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 layers without effecting a desensitization of said layers.

SUMMARY OF THE INVENTION

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

It is the object, according to one aspect of this invention, to provide stabilized photographic silver halides.

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

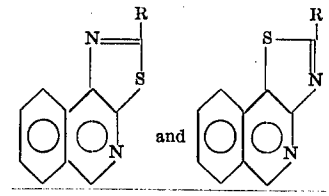
It is yet a further object to stabilize silver halide elements and emulsions without adversely affecting to any substantial degree, their photographic sensitivity.

It is a further object of this invention to provide photographic silver halides which are stabilized with a particular group of isoquinolines.

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 isoquinolines act as strong antifoggants and stabilize photographic silver halides without causing a serious reduction in the photographic sensitivity. The isoquinolines which have been found useful can be a thiazolo[5,4-c]isoquinoline, a thiazolo[4,5-c]isoquinoline, a 2-halo, hydroxy, thiol or aminothiazolo[5,4-c]isoquinoline or a 2-halo, hydroxy, thiol or amino[4,5-c]isoquinoline. The compounds are represented by the general formulas:



wherein each R can be hydrogen, halide, hydroxy, thiol or amino.

It is to be understood that the isoquinoline portion of the compounds of this invention can be substituted with any radical, such as alkyl radicals, aryl radicals, and the like, as long as such substitutions do not destroy the antifoggant properties of the compound. Examples of the isoquinolines are:

2-aminothiazolo[5,4-c]isoquinoline
2-aminothiazolo[4,5-c]isoquinoline
2-chlorothiazolo[5,4-c]isoquinoline
2-chlorothiazolo[4,5-c]isoquinoline
2-hydroxythiazolo[5,4-c]isoquinoline
2-hydroxythiazolo[4,5-c]isoquinoline
thiazolo[5,4-c]isoquinoline-2-thiol
thiazolo[4,5-c]isoquinoline-2-thiol

The compounds of this invention are conveniently prepared by the method described in Hall and Taurins, Can. J. Chem., 44, 2465, 2473 (1966).

The concentration of the stabilizing compounds can vary considerably depending on various factors such as the effects desired, silver content of the photographic elements, the nature of the particular silver halide, the degree of ripening, the location of the stabilizer in relation to the silver halide, the particular stabilizer, etc. In general, a concentration in the range of about 0.001 grams to about 10 grams of stabilizer per mole of silver halide is useful. A preferred range is from about 0.03 grams to about 0.5 grams of stabilizer per mole of silver halide. In accordance with the invention, one may use the higher concentrations without inducing a reduction in sensitivity. The optimum concentration of stabilizer for a particular photographic system 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 emulsion, 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 emulsion, and in accordance with the general practice organic solvents and diluents are preferred.

The light-sensitive silver halide emulsions 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. Pat. Nos. 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 hemicyanines. 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 being useful in orthochromatic, panchromatic and infrared emulsions, they are also useful in X-ray and other nonspectrally 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 bromoiodide, or silver chloroiodide 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. No. 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. 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 Carrol 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, a polyvinyl compound, acrylamide 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. 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. 30, 1965; and include the water-insoluble polymers of alkyl acrylates and methacrylates, acrylic acid, sulfoalkyl acrylates or methacrylates and the like.

The photographic emulsions 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 nonimage 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. 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.

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

EXAMPLES A–H

Compounds employed in this invention, listed in the table below, are incorporated, at concentrations listed in the table, into separate samples of a high-speed gelatino silver bromoiodide photographic emulsion. Each of the emulsions are coated on a cellulose acetate film support at a coverage of 459 mg. of silver and 1,040 mg. of gelatin per square foot. As a comparison film strips absent the compounds of this invention are also prepared. A sample of each film coating is exposed on an Eastman IB sensitometer, processed for five minutes in Kodak DK-50 Developer, fixed, washed and dried. Separate samples of the film coating are incubated for two weeks at 120° F. and 50 percent relative humidity before exposure and development. The results of the sensitometric tests on the fresh and incubated samples are summarized in the table.

TABLE I

Stabilizing compounds (g./mole of Ag)	Fresh samples			2 week incubation at 120° F., 50% relative humidity		
	Relative speed	Gamma	Fog	Relative speed	Gamma	Fog
None	100	1.50	.29	48	1.05	.83
A (0.12)	73	1.60	.10	80	1.30	.30
None	100	1.50	.22	48	0.88	.70
B (0.12)	78	1.48	.14	76	1.27	.24
C (0.12)	76	1.37	.15	80	1.25	.20
None	100	1.58	.14	39	1.03	.65
D (0.03)	97	1.43	.07	60	1.25	.16
None	100	1.42	.17	46	1.08	.83
E (0.03)	100	1.52	.17	83	1.33	.34
E (0.09)	97	1.48	.18	94	1.28	.28
F (0.12)	89	1.48	.17	76	1.32	.39
F (0.48)	68	1.45	.16	82	1.38	.16
G (0.12)	87	1.52	.19	57	1.28	.48
G (0.48)	76	1.45	.18	69	1.33	.30
H (0.12)	87	1.33	.17	100	1.30	.25
H (0.48)	67	1.20	.15	71	1.30	.17

A=2-aminothiazolo[5,4-c]isoquinoline.
B=2-chlorothiazolo[5,4-c]isoquinoline.
C=2-hydroxythiazolo[5,4-c]isoquinoline.
D=thiazolo[5,4-c]isoquinoline-2-thiol.
E=thiazolo[4,5-c]isoquinoline-2-thiol.
F=2-hydroxythiazolo[4,5-c]isoquinoline.
G=2-chlorothiazolo[4,5-c]isoquinoline.
H=2-aminothiazolo[4,5-c]isoquinoline.

The examples, as summarized in the table, show that the compounds of this invention are highly useful as stabilizers and fog inhibitors for photographic silver halides. It should be noted that fog is inhibited without any concurrent substantial loss, if any, in the photographic sensitivity of the silver halide emulsion. In the case of the incubated samples the speed of the treated emulsions is always greater than the nontreated samples. With respect to the fresh samples there was an insignificant loss in speed, if any.

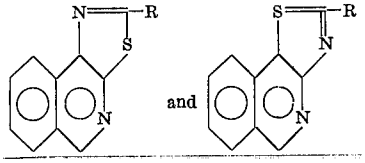
The invention, it is seen provides silver halide emulsions and elements stabilized with the particular antifoggants said antifoggants not causing any substantial deleterious effect upon speed or sensitivity.

The invention has been described scribed 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.

We claim:

1. A photographic element comprising a support, a silver halide layer and as a stabilizer a thiazolo[5,4-c]isoquinoline, a thiazolo[4,5-cisoquinoline, a 2-halo, hydroxy, thiol or aminothiazolo[5,4-c]isoquinoline or a 2-halo, hydroxy, thiol or aminothiazolo[4,5-c]isoquinoline.

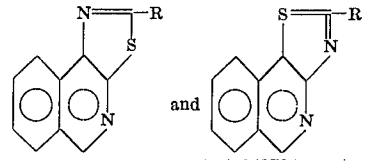
2. A photographic element comprising a support, a silver halide layer and as a stabilizer a compound having the formula selected from the group consisting of



wherein each R is hydrogen, halide, hydroxy, thiol or amino.

3. A photographic element as in claim **2** wherein said stabilizer is present in a concentration of from about 0.001 g. to about 10 g. per mole of silver halide.

4. A photographic silver halide emulsion comprising a stabilizing compound selected from the general formulas:



wherein each R is hydrogen, halide, hydroxy, thiol or amino, said stabilizing compound is present in a concentration of from about 0.001 to about 10.0 g. per mole of silver bromoiodide.

5. A photographic emulsion as in claim **4** wherein said stabilizing compound is present in a concentration of from about 30 mg. to about 0.5 g. per mole of silver halide.

6. A photographic emulsion as in claim **4** wherein said stabilizer is 2-aminothiazolo[5,4-c]isoquinoline or 2-aminothiazolo[4,5-c]isoquinoline.

7. A photographic emulsion as in claim **4** wherein said stabilizer is 2-chlorothiazolo[5,4-c]isoquinoline or 2-chlorothiazolo[4,5-c]isoquinoline.

8. A photographic emulsion as in claim **4** wherein said stabilizer is 2-hydroxythiazolo[5,4-c]isoquinoline or 2-hydroxythiazolo[4,5-c]isoquinoline.

9. A photographic emulsion as in claim **4** wherein said stabilizer is thiazolo[5,4-c]isoquinoline-2-thiol or thiazolo[4,5-c]isoquinoline-2-thiol.

10. A photographic silver halide emulsion as in claim **4** wherein said silver halide emulsion is a high-speed gelatino silver bromoiodide emulsion.

11. A method for stabilizing photographic silver halide against fog which comprises contacting said silver halide with a stabilizing compound having a formula according to claim **1**.

* * * * *

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,630,745 Dated December 28, 1971

Inventor(s) Dorothy J. Beavers, et al.

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

Title page, item [54], line 2, "IOSQUINOLINE" should read ---ISOQUINOLINE---.

Column 1, line 2, "IOSQUINOLINE" should read ---ISOQUINOLINE---.

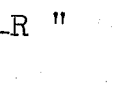
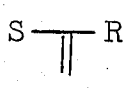
Column 4, line 69, under heading "Stabilizing compounds (g./mole of Ag)", "E(0.00)" should read ---E (0.09)---.

Column 5, line 14, "scribed" should be deleted.

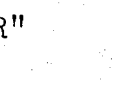
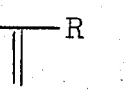
In The Claims

Column 5, line 21, that part of formula reading "[4,5-cisoquinoline should read ---[4,5-c]isoquinoline---.

Column 5, line 28, that part of formula set forth as:

"  " should be ---  ---.

Column 6, line 3,

"" should read --- ---.

Signed and sealed this 17th day of October 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents