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PHOTOGRAPHIC ELEMENTS HAVING THIAZOLIDINE COMPOUNDS IN LIGHT-INSENSITIVE LAYERS

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U.S. Cl. 96—67 7 Claims

ABSTRACT OF THE DISCLOSURE

Photographic elements having a radiation-sensitive, colloid-silver halide emulsion layer and a contiguous light insensitive stratum containing a thiazolidine compound, preferably L-thiazolidine-4-carboxylic acid.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to photography and to photographic elements with improved ratios of speed (or light sensitivity) to fog.

Description of the prior art

The use of L-thiazolidine-4-carboxylic acid in photographic developer solutions is disclosed as a fog inhibitor in Spath, U.S. 2,860,976. Pierre Glafkides on page 287 of Photographic Chemistry, Fountain Press, London, 1958, mentions thiazolidine-4-carboxylic acid as obtainable from gelatin and capable of functioning as a contrast modifier.

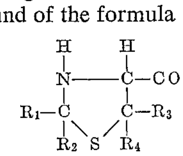
A number of references in Chemical Abstracts relate to the addition of various 4-carboxythiazolidine derivatives to photographic emulsions as fog inhibitors:

Chem. Abstracts, 44, 1490a (1950)
Chem. Abstracts, 46, 2937c (1952)
Chem. Abstracts, 46, 10025a (1952)
Chem. Abstracts, 47, 1514g (1953)
Chem. Abstracts, 47, 6803e (1953)
Chem. Abstracts, 48, 11394b (1954)
Chem. Abstracts, 49, 15575h (1955)

The use of the thiazolidine compound in a light-insensitive layer contiguous with a light-sensitive silver halide layer improves the speed-to-fog ratio.

SUMMARY OF THE INVENTION

The photographic element of this invention comprises a support, a light-sensitive layer comprising silver halide in a hydrophilic colloid binder, and in operative association therewith, a light-insensitive layer containing a thiazolidine compound of the formula



(I)

where the R's (which may be the same or different) are H, alkyl of 1–4 carbons, e.g., CH_3, C_2H_5, C_3H_7, C_4H_9 or aryl, e.g., phenyl.

The particularly preferred thiazolidine compound is L-thizaolidine - 4 - carboxylic acid which will subsequently be referred to as TCA.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In a preferred embodiment, a thiazolidine compound of Formula I, e.g., TCA, is incorporated in the anti-

abrasion layer of any conventional photographic element. The compound may be present in another light-insensitive layer adjacent to the silver halide layer, e.g., in the substratum layer, filter layer, nonhalation layer or separator layer, but as stated above preferably is in an antiabrasion layer contiguous with a silver halide layer.

The silver halide emulsion may be of any of the usual types (black and white or color) such as those employed for medical or industrial X-ray, cine, graphic arts or portrait use. The silver halide crystal may also be any one of the usually types such as silver chloride, silver bromide, silver bromochloride or silver iodobromide. Particularly useful results have been obtained with high speed medical X-ray films containing silver iodobromide crystals. Gelatin is the preferred binder for the silver halide crystals but it may be partially or completely replaced with other natural or synthetic binders as known in the art. Thus, binders used to improve covering power, e.g., dextran, dextrin, polyvinyl pyrrolidone, etc. as well as latices of polymers such as polyethylacrylate which are useful in improving dimensional stability are advantageously included in many types of silver halide emulsions employed according to this invention.

The range of concentration of the thiazolidine compound of Formula I depends somewhat on the emulsion, a higher concentration being desirable as the silver halide molar surface area increases (i.e., as the emulsion sensitivity decreases). The concentration is best expressed in terms of the quantity of compound contained in an area of the light-insensitive layer adjacent to an area of the light-sensitive layer containing one mole of silver halide. Generally, a useful range of concentration of the thiazolidine compound is from 0.0005 to 0.5 millimole per mole of silver halide with a preferred range being from 0.001 to 0.1 millimole. Concentrations are expressed in terms of the amount of the thiazolidine compound present in an area of the light-insensitive layer corresponding to the area of the silver halide emulsion layer containing one mole of silver halide.

The light-insensitive layer containing the thiazolidine compound, which is normally the antiabrasion layer, conveniently has gelatin as the binder. However, the gelatin could be replaced, totally or in part, with other hydrophilic colloid binders, as stated above. A typical antiabrasion layer is coated from an aqueous solution of gelatin containing the thiazolidine compound, coating aids and gelatin hardeners such as aldehydes, e.g., formaldehyde and glutaraldehyde, glyoxal, mucochloric acid, and chrome alum. From economic considerations, the coating is applied as a very thin layer, e.g., about 10 mg./dm.^{2} of gelatin. Since the thiazolidine compound apparently should migrate into the silver halide layer to be effective, a thicker light-insensitive layer would require a higher concentration of the thiazolidine compound for a given concentration to reach the silver halide layer.

The support for the photographic element preferably is a polyethylene terephthalate film base as described in Alles et al. U.S.P. 2,627,088, Feb. 3, 1953 but other coated and uncoated supports including those listed in Cohen et al. U.S.P. 3,252,801, May 24, 1966 can be used. Any of the usual emulsion adjuvants may be present in the silver halide layer, e.g., emulsion sensitizers, sensitizing dyes, coating aids, etc.

The invention will be further illustrated by but is not intended to be limited to the following examples:

Example I

A high-speed gelatino-silver iodobromide emulsion containing 1.2 mole percent silver iodide and 98.8 mole percent silver bromide was made in the usual manner and then coagulated and washed as taught in Moede, U.S.

2,772,165. Following the washing step, the emulsion was redispersed in water together with gelatin. The emulsion was digested with organic sulfur and gold thiocyanate to give optimum sensitivity. Post-sensitization additives of a conventional nature were added and the emulsion was coated on a 0.007-inch thick polyethylene terephthalate film support bearing a thin gelatin layer over a subcoat of a copolymer of vinylidene chloride/methyl acrylate/itaconic acid admixed with a homopolymer of ethyl acrylate described in Example I of assignee's Rawlins application Ser. No. 494,257 filed Oct. 8, 1965 (U.S.P. 3,443,950, May 13, 1969).

Over a portion of this film was coated a 2.6% by weight aqueous gelatin solution containing conventional coating aids and formaldehyde and chrome alum hardening agents. This control antiabrasion layer was applied at a coating weight of 10 mg./dm.^{2} of gelatin. Two other portions of the film were overcoated with a similar antiabrasion layer but which contained TCA in the amounts indicated in the table below. Samples of the coatings were given a medical X-ray standard speed screen exposure at 70 kvp. and 4 milliamps for 5 sec. through a $\sqrt{2}$ aluminum step wedge. The exposed samples were developed for 3 minutes at 68° F. in the following X-ray developer to determine sensitometric properties.

	G.
p-Methylaminophenol sulfate	3.0
Anhydrous sodium sulfite	50.0
Hydroquinone	9.0
Anhydrous sodium carbonate	50.0
Potassium bromide	4.9
Water to make 1000 ml.	

TABLE I.—SENSITOMETRIC PROPERTIES

TCA overlying one mole of silver halide	Rel. speed	Gradient	Fog
None (control)	100	2.24	.07
1.43 mg	102	2.06	.07
14.3 mg	142	2.31	.09

Example II

A very high-speed gelatino-silver iodobromide emulsion with 1.8 mole percent silver iodide and 98.2 mole percent silver bromide was precipated, ripened, washed according to U.S. 2,772,165, redispersed, digested, and coated in a conventional manner. The resulting film was overcoated with antiabrasion layers, exposed, and processed as in Example I to give the following results:

TABLE II.—SENSITOMETRIC PROPERTIES

TCA overlying one mole of silver halide	Rel. speed	Gradient	Fog
None (control)	100	2.60	.06
0.19 mg	114	2.51	.04
0.38 mg	127	2.46	.04
0.76 mg	122	2.26	.03
1.52 mg	116	2.20	.05

Example III

A medium speed gelatino-silver iodobromide emulsion containing 1.2 mole percent silver iodide and 98.8% silver bromide was made in the usual way and freed of excess salts by chilling, noodling, and washing. The emulsion was then digested to optimum sensitivity with gold and sulfur sensitization. Next the emulsion was coated on film base as described in Example I and overcoated with antiabrasion layers containing the below-indicated amounts of TCA. Samples of the films were given an industrial X-ray lead through screen exposure at 200 kvp. and 4 milliamps for 1 minute through a $\sqrt{2}$ aluminum step wedge. The films were developed for 5 minutes at 68° F. in the developer solution of Example I.

TABLE III.—SENSITOMETRIC PROPERTIES

TCA overlying one mole of silver halide	Rel. speed	Gradient	Fog
None (control)	100	2.33	.00
7.15 mg	105	2.49	.19

Example IV

A gelatino-silver bromochloride lithographic type emulsion containing 30 mole percent silver bromide and 70 mole percent silver chloride was made in the usual manner and digested with gold and sulfur to increase its sensitivity. After post-sensitization additions, including the addition of a polyethyl acrylate latex to improve dimensional stability, the emulsion was coated on the film support of Example I and dried. A portion of the coated emulsion was overcoated with an antiabrasion layer as described in Example I and two portions were overcoated with similar antiabrasion coatings containing the indicated amount of TCA. Samples of the films were given a 1/10,000 sec. exposure with a xenon flash through a $\sqrt{2}$ step wedge at a distance of 6⅜ inches. The exposed samples were developed for 4 minutes at 74° in the developer of Example I.

TABLE IV

TCA overlying one mole of silver halide	Rel. speed	Fog
None (control)	100	.04
23.6 mg	250	.04
47.7 mg	300	.04

Example V

Example I was essentially repeated except that the antiabrasion layers contained various thiazolidine compounds in the concentrations indicated in the table below:

TABLE V

Thiazolidine compound	Quantity, mg.[1]	Rel. speed	Gradient	Fog
None (Control)		100	3.00	.09
Penicillamine	2.0	105	3.10	.09
Do	16.0	112	3.26	.11
TCA	14.3	135	3.11	.11

[1] Overlying one mole of silver halide.

Example VI

An aqueous 3% by weight solution of gelatin was divided into two portions. To one there was added an aqueous solution of 2,2,5,5-tetramethyl-L-thiazolidine-4-carboxylic acid while to the other portion, serving as a control, there was added an equal quantity of distilled water. The solutions were coated as sub-stratum layers on film base as in Example I to coating weights of about 10 mg./dm.^{2} of gelatin. Both films were then overcoated with the silver halide emulsion layer and then further overcoated with the control antiabrasion layer of Example I. Thus, there resulted an experimental coating with a sub-stratum layer containing a thiazolidine compound in a concentration of 1.86 mg. per area of adjacent silver halide emulsion layer containing one mole of silver halide.

Both films were exposed and processed as in Example I giving the results below:

	Rel. speed	Fog
Control	100	.06
Sampling containing thiazolidine compound in sub-stratum layer	106	.05

Example VII

A fine grain, medium-speed, gelatino-silver halide emulsion having a silver halide composition of 96.8 mole percent silver bromide and 3.2 mole percent silver iodide was made by precipitation in the usual manner. The precipitated emulsion was coagulated and washed as described in Example I. The sensitivity of the emulsion was increased by addition of a gold salt and a sulfur sensitizer and by digestion of the modified emulsion. Following digestion, post-sensitization additives and stabilizers, e.g., KBr, antifoggants, etc., were added along with polymers as described in Cohen et al. U.S.P. 3,252,801 to improve covering power and dimensional stability. The emulsion was divided into four equal portions and TCA was added to three of the portions. The emulsions were coated on the photographic film base of Example I. A standard gelatin antiabrasion layer was applied to all samples which, after drying, were given a 20-second exposure to a white light from a tungsten filament lamp through an intensity scale sensitometric step wedge. The exposure in each successive step increased by a factor of the 4th-root-of-2. The exposed samples were developed for 3 minutes in a continuous tone developer containing the developing agents set forth in Example I and the results are shown in the following table:

	Rel. speed	Fog
Grams of TCA per mole of silver halide:		
None	100	0.06
0.0015	100	0.07
0.015	109	0.09
0.150	117	0.43

Strips of the control material having the same exposure were again developed in portions of the continuous tone developer to which solid portions of TCA were added with the results shown in the following table:

	Rel. speed	Fo
Grams of TCA per liter of developer:		
None	100	0.06
0.001	100	0.05
0.010	104	0.07
0.10	101	0.16

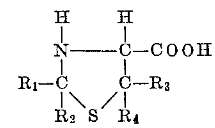
Two additional photographic films bearing coatings made from an emulsion as described above but free from TCA were made. A standard gelatin antiabrasion overcoating was applied over one of the emulsion coatings to serve as a control. To the other there was applied a similar antiabrasion overcoating which contained TCA in a concentration sufficient to provide 14.4 mg. of this agent per mole of silver halide in the adjacent layer. The results were as follows:

	Rel. speed	Fog
Control	100	.06
Experimental overcoating with TCA	127	.06

The thiazolidine compounds, when present in a light-insensitive layer, are valuable in improving the speed-to-fog ratio of photographic elements. This improvement may result from an increase of speed, a decrease of fog, or a combination of the two. Such effects, particularly the speed increases, are surprisingly dependent on the location of the thiazolidine compound in a light-insensitive layer of the element rather than in the silver halide stratum itself or even in the developer. An additional beneficial effect in the elements of the present invention has been observed as a distinct improvement in the stability of the latent image. Although TCA appears to be a definitely preferred material, various other thiazolidine compounds defined by the above formula have been tested and found to give similar improvements when used according to this invention.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A photographic element comprising
(1) a support
(2) a radiation-sensitive, colloid-silver halide emulsion layer, and in operative association therewith
(3) a light-insensitive contiguous, hydrophilic colloid layer containing a thiazolidine compound of the formula:



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wherein each of R_1, R_2, R_3 and R_4 is H, alkyl of 1–4 carbons or aryl in an amount of 0.0005 to 0.5 millimole per mole of silver halide.

2. An element according to claim 1 wherein layer (3) is contiguous with layer (2).

3. An element according to claim 1 wherein layer (3) is an outer anti-abrasion layer contiguous with layer (2).

4. An element according to claim 1 wherein layers (2) and (3) contain gelatin as a binding agent.

5. An element according to claim 1 wherein said compound is 2,2,5,5-tetramethyl-L-thiazolidine - 4 - carboxylic

6. An element according to claim 1 wherein said compound is 2,2,5,5-tetramethyl-L-thiazolidine-4-carboxylic acid.

7. An element according to claim 1 wherein said support is a thin flexible hydrophobic film support.

References Cited

UNITED STATES PATENTS

2,860,976	11/1958	Spath	96—109X
2,860,985	11/1958	Dann et al.	96—109X

OTHER REFERENCES

Chemical Abstract, vol. 49, 15575h (1955).

NORMAN G. TORCHIN, Primary Examiner

R. E. FICHTER, Assistant Examiner

U.S. Cl. X.R.

96—109

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,565,625 Dated FEB. 23, 1971

Inventor(s) CHARLES LAWRENCE SCAVRON

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

Col. 6, claim 5, last line, "2,2,5,5-tetramethyl-L-thiazolidine-4-carboxylic" should read --L-thiazolidine-4-carboxylic acid.--

Signed and sealed this 10th day of August 1971.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

WILLIAM E. SCHUYLER, J
Commissioner of Patent