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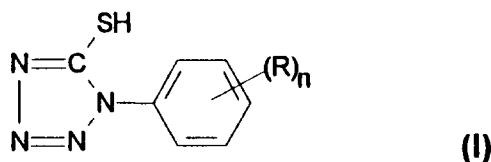
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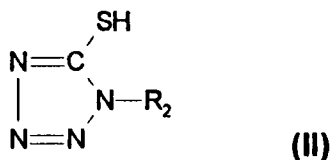
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I-17016 Ferrania, Savona (IT)**(54) **Silver halide photographic element and method for stabilizing a light-sensitive silver halide emulsion**

(57) Method for stabilizing a photosensitive silver halide emulsion which comprises the following steps, in sequence:

- adding to said emulsion a water-soluble bromide salt;
- spectrally sensitizing said emulsion;
- adding to said spectrally sensitized emulsion a compound having the following formula (I):



wherein R represents nitro, cyano, fluoroalkyl, halogen, -COOR₁ group, R₁ being hydrogen or an alkyl group, and n is an integer from 1 to 5; or having the following formula (II):



wherein R₂ is a branched alkyl chain having from 3 to 5 carbon atoms.

Light-sensitive silver halide photographic element comprising a support bearing at least one light-sensitive silver halide emulsion layer comprising a water-soluble bromide salt and a compound having previous formula (I) or (II).

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Description

BACKGROUND OF THE ART

5 It is known in the art to stabilize silver halide emulsions with respect to shelf stability with an azaindene compound as illustrated, for example, in US 2,444,607; 2,444,609; 2,449,225 and 2,450,397.

US 2,772,164; 2,835,581; 3,333,961 describe chemically or optically sensitized silver halide emulsions, as antifog-
gants containing specified classes of triazaindenes, tetrazaindenes and pentazaindenes.

10 US 3,418,130; 3,462,272 and 3,563,755 are directed to silver halide emulsions as antifoggants containing specified classes of tetrazaindenes, added after chemical or physical digestion. Photographic materials stabilized with tetrazaindene derivatives show acceptable sensitometric characteristics immediately after coating, but unacceptable keeping properties, with a decrease of contrast values and an increase of speed and Dmax values.

15 T.H.James, "*The Theory of the Photographic Process*", 4th edition, p. 396 reports several compounds acting as antifoggants and stabilizers. Among the inorganic compounds listed, the most useful ones include soluble bromides, complex salts of group VIII of the periodic table, and salts of mercury, cadmium, zinc and manganese. A large number of organic compounds have been also described therein, such as, for example, triazoles, tetrazoles, benzotriazoles, oxazoles, thiazoles, nitrobenzimidazoles, nitroindazoles, some compounds containing the -SH group, and the like.

20 Silver halide photographic red-sensitive materials are particularly suitable for exposures in the range from about 600 nm to about 700 nm, for example, with exposures with He-Ne (633 nm) and red diode (650, 670 nm) lasers. Said red-sensitive materials contain silver halide emulsions, generally silver chlorobromide emulsions having a large content of silver chloride (e.g., more than 50% moles, preferably more than 60% moles), and having an average grain size equal or lower to 0.30 μm .

25 Said red-sensitive materials must be stabilized to maintain good sensitometric properties after long term storage. This is a particular problem for this kind of materials. These materials show good sensitometric values for speed and contrast values on fresh materials, obtained for example with the addition of soluble halides, but they also show an undesired change in said values during keeping. On the other side, said red-sensitive materials can show good keeping properties when stabilized with tetrazole derivative compounds, but the speed on the fresh materials is too low.

30 US 4,332,888 describes a method for stabilizing a photosensitive silver halide emulsion by a) providing sufficient stabilizer to the emulsion to stop chemical ripening without interfering with spectral sensitization, b) spectrally sensitizing said emulsion and c) adding to said emulsion a water soluble bromide salt, 1-phenyl-5-mercaptotetrazole compound and a stabilizer selected from the group consisting of a hydroxytriazaindene, an aminotriazaindene, a hydroxytetrazaindene, an aminotetrazaindene, a hydroxypentazaindene and an aminopentazaindene. Preferably, the stabilizer in step a) is the same as in step c), however any material which will stop chemical ripening may be employed. Said method provides a degree of short term stability to the emulsion during the spectral sensitization. The long term stability is then
35 provided subsequent to spectral sensitization with the introduction of said combination of stabilizers in step c). The emulsion disclosed in said patent is chloride free and contains 6% of iodide and 94% of bromide, and it is particularly useful for color diffusion transfer film units and silver diffusion transfer film units.

40 US 4,536,473 describes a light-sensitive material comprising emulsion layers with silver halide grains containing at least silver chloride, the material being sensitized to infrared radiation with a tricarbocyanine or a dicarbocyanine dye. The emulsion layer contains from 0.0003 to 0.01 mole per silver mole of a water-soluble bromide, such as ammonium bromide, potassium bromide, sodium bromide and lithium bromide, added after the addition of the spectral sensitizing dye.

45 US 4,794,070 discloses a photographic element comprising a base layer and at least a silver halide photographic emulsion on one side of said base, the element containing at least one layer which is free of silver halide and contains at least 0.1 gram per square meter of bromide ions as an aqueous alkaline soluble bromide salt. The emulsion is sensitized to infrared radiation. The addition of said bromide salt into radiographic elements reduces the developer chemistry fluctuations.

50 US 4,786,588 discloses silver halide particles which are transhalogenated by adding thereto a specified amount of water-soluble bromide just before or during sulfur sensitization, to obtain a sulfur-sensitized silver halide emulsion of high sensitivity. If the sulfur sensitizer is added to the emulsion after a long period of time from the addition of the water-soluble bromide, said addition of water-soluble bromide is almost ineffective for elevation of the sensitivity. On the contrary, if the water-soluble bromide is added to the emulsion after the complete ripening thereof to achieve the maximum sensitivity by the previous addition of the sulfur sensitizer to the emulsion, the sensitivity of the emulsion is not elevated, but is rather lowered.

55 US 5,068,167 describes a high contrast photographic material comprising a silver halide emulsion in association with a hydrazine, said material having reduced fog due to the presence of water-soluble bromide and/or water-soluble chloride added to the emulsion at any suitable stage during preparation. Addition is generally made after the washing stage and may conventionally be added together with any sensitizing dye.

US 4,830,958 describes a color light-sensitive photographic material which is excellent in rapid processability and has little sensitivity variation caused by a change on standing in the preparation of the material. It comprises at least one silver halide emulsion layer containing highly chloride-containing silver halide grains, a water-soluble bromide and a high boiling organic solvent to disperse a photographic coupler. The water-soluble bromides may be added at any point of time from the completion of the chemical ripening of a silver halide emulsion to the coating of the emulsion.

European Patent Application 440,947 discloses silver halide photographic elements sensitive to infrared radiation, wherein at least one infrared sensitized emulsion layer is associated with a 1-aryl-5-mercaptotetrazole group substituted in the aryl group by at least one electron-attracting group, such as for example a fluoroalkyl group.

Japanese Patent application No. 04-329,536 discloses a silver halide photographic emulsion supersensitized by a phenylmercaptotetrazole compound having at least a trifluoromethyl group as a substituent of the benzene ring. Said supersensitizer is dissolved in a solvent and added to the emulsion, before or after the addition of a sensitizer.

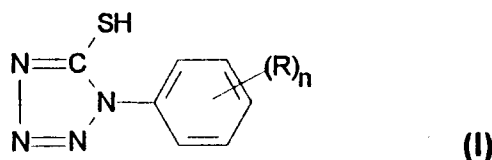
It could be useful to have photographic elements showing good initial sensitometric values, in particular related to speed values, and good keeping properties, related to speed and contrast values.

It could be also useful to add the stabilizing agents before the spectral sensitization, to allow the photographic element to immediately reach a good stability, without negative effects on sensitometric properties.

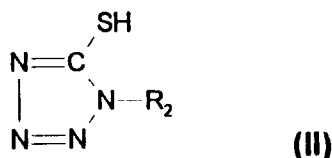
SUMMARY

A method for stabilizing a photosensitive silver halide emulsion which comprises the following steps, in sequence:

- a) adding to said emulsion a water-soluble bromide salt;
- b) spectrally sensitizing said emulsion;
- c) adding to said spectrally sensitized emulsion a compound having the following formula (I):



wherein R represents nitro, cyano, fluoroalkyl, halogen, $-\text{COOR}_1$ group, R_1 being hydrogen or an alkyl group, and n is an integer from 1 to 5; or having the following formula (II):



wherein R_2 is a branched alkyl chain having from 3 to 5 carbon atoms.

The method of the present invention provides photographic elements showing good initial sensitometric values and good keeping properties, in particular with reference to speed and contrast values.

In an other aspect, the present invention refers to a light-sensitive silver halide photographic element comprising a support bearing at least one light-sensitive silver halide emulsion layer comprising a water-soluble bromide salt and a compound of previous formula (I) or (II).

DETAILED DESCRIPTION OF THE INVENTION

In stabilizing a photosensitive silver halide emulsion, water-soluble bromide salts include various compounds capable of dissociating to a bromide in water. For example, a salt of bromide such as ammonium bromide, potassium bromide, sodium bromide, lithium bromide, etc. can be employed. Also, an appropriate organic bromide, for example tetraethylammonium bromide, ethylpyridinium bromide, etc. can be also used. Among the bromide salts, however, cadmium bromide and zinc bromide, etc. are poisonous when they are excessively absorbed by human body. Therefore, biologically harmless (non-toxic) water-soluble bromides are preferred as described above.

The water-soluble bromide to be added to the silver halide emulsion is used in an amount sufficient to substantially increase the sensitivity of the emulsion and/or to substantially prevent any change in sensitivity while time passing. The amount of water-soluble bromide can be varied in a wide range and, particularly preferred results can be obtained when the bromide is added prior to spectral sensitization in an amount of from about 0.05 to about 2 millimoles per silver mole, preferably from about 0.2 to about 1.70 millimoles per silver mole.

Said water-soluble salts must be added before spectral sensitization to obtain better sensitometric results, in particular higher speed on the fresh material, and to reduce the variation of said sensitometric values on incubation test.

After said water-soluble salts have been added to the emulsion, the emulsion is spectrally sensitized. The spectral sensitizers used in the present invention are those commonly known in the art which are suitable for exposure in the range from about 620 nm to about 680 nm, for example with He-Ne (633 nm) and red diode (650, 670 nm) laser exposures. Useful spectral sensitizers are, for example, trinuclear merocyanine dyes having a benzothiazole or benzoselenazole group described in US 5,116,722, merocyanine spectral sensitizing dyes containing at least two acid groups disclosed in CH Patent Application No. 677,409, benzimidazole pentacarbocyanine spectral sensitizing dyes described in US 4,717,650, dyes containing a quinoline group described in US 4,336,323, and trinuclear merocyanine dyes disclosed in EP 607,478 and in the pending European Patent application Ser. No. 93115561.8.

Spectral sensitizing dyes used in the present invention can be prepared according to procedures well-known in the art, such as those described in James, *The Theory of Photographic Processes*, MacMillan, 4th edition, 1977.

Spectral sensitizing dyes used in the present invention are incorporated in the silver halide photographic emulsion in a content of from 0.01 to 0.20 grams/silver mole, preferably from 0.02 to 0.16 grams/silver mol.

The spectral sensitizing dyes useful in the present invention can be directly dispersed in the emulsion. Alternatively, they may be first dissolved in a suitable solvent, such as methyl alcohol, methylcellosolve, acetone, water, pyridine or a mixture thereof and then added to the emulsion as a solution. Processes for adding the sensitizing dyes to the photographic emulsion are described for example in US 3,469,987; 3,676,147; 3,822,135; 4,199,360 and in US 2,912,343; 3,342,605; 2,996,287 and 3,429,835. The above mentioned sensitizing dyes may be uniformly dispersed in the silver halide emulsion prior to the coating thereof onto a suitable support base. Of course, the dispersion procedure can be performed in any suitable step of the silver halide emulsion preparation.

Any silver halide photographic emulsion type can be used in the practice of the present invention. Silver chloride, silver bromide, silver iodobromide, silver chlorobromide, silver chloriodobromide and mixtures thereof can be used, for instance, dispersed in a hydrophilic colloid or binder. Any configuration of grains, cubic, orthorhombic, hexagonal, epitaxial, or tabular (high aspect ratio) grains may be used. The colloid may be partially hardened or fully hardened by any of the variously known photographic hardeners. Such hardeners are free aldehydes, aldehyde releasing compounds, triazines and diazines, aziridines, vinylsulfones, carbodiimides, and the like may be used, as described, for example, in US 3,232,764; 2,870,013; 3,819,608; 3,325,287; 3,992,366; 3,271,175 and 3,490,911.

In addition, in the course of formation of silver halide grains or in the process of physical ripening, there may be added to the silver halide emulsion a cadmium salt, sulfite, lead salt, thallium salt, rhodium salt or rhodium complex salt, iridium salt or iridium complex salt, ruthenium salt or ruthenium complex salt, or the like.

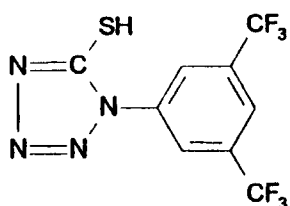
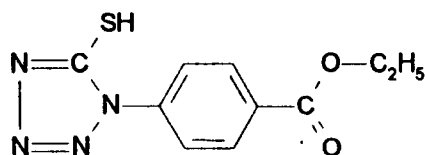
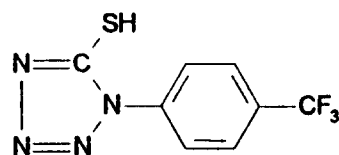
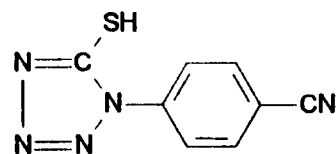
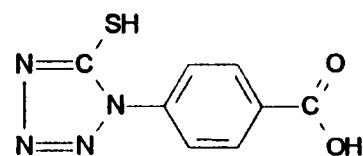
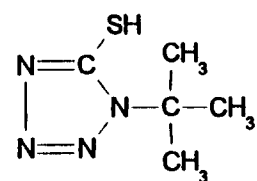
In the previous formula (I), R may be nitro, cyano, fluoroalkyl, halogen (preferably, chlorine or bromine) or a COOR₁ group, wherein R₁ is hydrogen or an alkyl group having 1 to 5 carbon atoms (such as, for example, methyl, ethyl, n-butyl, etc); and n is an integer from 1 to 5.

Preferably, in the previous formula (I), R is a straight or branched fluoroalkyl group having 1 to 4 carbon atoms, wherein the alkyl group has at least one fluorine atom per carbon, preferably at least 1.5 fluorine atom per carbon, more preferably all hydrogen atoms substituted with fluorine atoms.

When the term "group" or "ring" is used in the present invention, the described chemical material includes the basic group or ring and that group or ring with conventional substituents. When the term "moiety" is used, only an unsubstituted chemical material is intended to be included. For example, "alkyl group" includes not only such alkyl moieties as methyl, ethyl, octyl, stearyl, etc., but also such moieties bearing substituent groups such as halogen, cyano, hydroxyl, nitro, amine, carboxylate, etc. On the other hand, "alkyl moiety" includes only methyl, ethyl, octyl, stearyl, cyclohexyl, etc.

In the previous formula (II), R₂ is a branched alkyl chain having from 3 to 5 carbon atoms, preferably is a t-butyl.

Practical examples of compounds of formulas (I) and (II) are illustrated below, but the invention is not limited to these compounds.

**Compound 1****Compound 2****Compound 3****Compound 4****Compound 5****Compound 6**

The compounds of formula (I) are added to the silver halide photographic emulsion in an amount of from about 0.05 to about 2.0 millimoles per silver mole, preferably from about 0.20 to about 1.70 millimoles per silver mole.

The silver halide emulsions may be chemically sensitized using the usual sensitizing agents. Sulfur containing compounds, gold and noble metal compounds, polyoxyalkylene compounds are particularly suitable. Methods for chemically sensitizing silver halide emulsions are described, for example, in Research Disclosure 17643, Section III, 1978.

Other conventional photographic addenda such as coating aids, antistatic agents, acutance dyes, antihalation dyes and layers, antifoggants, latent image stabilizers, supersensitizers, antikinking agents, high intensity reciprocity failure reducers, plasticizers, matting agents, developing agents, color couplers, absorbing and scattering materials, which may be added to the silver halide emulsions are described in Research Disclosure 17643, 1978.

Gelatin is generally used as hydrophilic colloid for the silver halide photographic elements of the present invention. As hydrophilic colloids, gelatin derivatives, natural substances such as albumin, casein, agar-agar, alginic acid and the

like, and hydrophilic polymers such as polyvinyl alcohol, polyvinylpyrrolidone, cellulose ethers, partially hydrolyzed polyvinyl acetate, and the like can be used in addition to or instead of gelatin. Further, gelatin can be partially substituted with polymer latexes obtained by emulsion polymerization of vinyl monomers, such as polyethylacrylate latexes, to improve the physical characteristics of the photographic layers.

The support base used in the silver halide photographic elements of this invention can be any of the conventionally used support bases, such as glass, cloth, metal, film including for example cellulose acetate, cellulose acetate-butyrate, cellulose nitrate, polyester (such as for instance, polyethylene terephthalate or polyethylene naphthalate), polyamine, polystyrene, and the like, paper including baryta, coated paper, resin-coated paper, and the like.

The silver halide emulsions according to the present invention may be used as photosensitive emulsions for various photographic elements, such as high surface sensitivity or high internal sensitivity negative emulsions, surface-fogged or unfogged direct-positive emulsions, print-out emulsions, reversal emulsions, emulsions for black-and-white materials, for color materials, radiographic materials, color transfer materials, and the like.

The photographic elements according to this invention may be processed to form a visible image upon association of the silver halides with an alkaline aqueous medium in the presence of a developing agent contained in the medium or in the photographic elements, as known in the art. In the case of color photographic elements, the processing comprises at least a color developing bath and, optionally, a prehardening bath, a neutralizing bath, a first (black and white) developing bath, etc. These and other baths which complete the photographic processing (e. g., bleaching, fixing, bleach-fixing, intensifying, stabilizing and washing baths) are well known in the art and are described for instance in Research Disclosure 17643, 1978.

The present invention is now illustrated by reference to the following examples.

EXAMPLE 1

A monodispersed cubic silver chlorobromide emulsion (64% chloride, 36% bromide) was prepared, having an average size of 0.28 μm and being doped with iridium and ruthenium compounds in an amount of 0.3 and 0.6 mole per silver mole, respectively. The emulsion was then chemically sensitized with gold, thiosulfate and p-toluene-thiosulfonate and stabilized with a 2-methylthio-4-methyl-6-hydroxy-triazaindolizine.

The emulsion was then spectrally sensitized with a trinuclear merocyanine dye having a maximum absorbance at 569 and 608 nm in methyl alcohol solution. A coating was then prepared by coating the emulsion onto a polyvinylidene chloride subbed polyester base at a silver coverage of 4.3 g/m² (Sample 1).

Samples 2 to 10 were prepared as Sample 1, by adding however potassium bromide salts before the addition of the spectral sensitizing dye and then Compound (1) of the present invention after the addition of the spectral sensitizing dye, in the amounts reported in Table 1.

Table 1

Samples	KBr moles per 100 Ag moles	Compound 1 mmoles/Ag mole
1 (reference)	0	0
2 (comparison)	0.5	0
3 (comparison)	1	0
4 (comparison)	1.5	0
5 (comparison)	0	0.26
6 (comparison)	0	0.38
7 (comparison)	0	0.50
8 (comparison)	0	0.73
9 (invention)	0.6	0.50
10 (invention)	1	0.40

The samples were evaluated after exposure with a 670 nm red diode laser for a dwell time of 10^{-6} seconds and development in 3M RDC V rapid access chemistry for 30 seconds at 32°C. Table 2 shows the results obtained on fresh coated materials. Table 3 shows the percentage of variation of sensitometric values obtained after incubation test (5 days at 50% RH, at 60°C). Sensitometric results include Dmin, Speed, Average and Shoulder contrast. The higher the contrast, the better the dot quality of the image thus obtained. Dmin is the lowest density value on exposed side of fiducial mark and Speed is measured in Log 20/E (E expressed in lux-seconds), at density of 0.20 above Dmin. The toe contrast

corresponds to the absolute value of the slope of the line joining the density points of 0.07 and 0.17 above Dmin. The average contrast corresponds to the absolute value of the slope of the line joining the density points of 0.10 and 2.50 above Dmin and the shoulder contrast corresponds to the absolute value of the slope of the line joining the density points of 1.60 and 4.00 above Dmin.

Table 2

Samples	Dmin	Sensitivity	Toe Contrast	Average Contrast	Shoulder Contrast
1 (reference)	0.03	3.55	1.27	8.57	12.0
2 (comparison)	0.03	3.62	1.22	7.65	13.8
3 (comparison)	0.03	3.61	1.25	7.65	14.7
4 (comparison)	0.03	3.57	1.07	7.21	12.4
5 (comparison)	0.03	3.49	1.37	8.38	10.3
6 (comparison)	0.03	3.49	1.30	8.40	9.6
7 (comparison)	0.03	3.47	1.25	9.10	9.4
8 (comparison)	0.03	3.43	1.17	8.25	8.3
9 (invention)	0.03	3.55	1.32	8.11	11.3
10 (Invention)	0.03	3.55	1.33	7.87	11.2

Table 3

Samples	% Dmin	% Sensitivity	% Toe Contrast	% Average Contrast	% Shoulder Contrast
1 (reference)	+ 266	+ 4.0	- 53	- 20	- 21
2 (comparison)	+ 33	+ 1.0	- 38	- 12	- 20
3 (comparison)	0	0	- 34	- 15	- 23
4 (comparison)	0	- 1.2	- 25	- 16	- 16
5 (comparison)	0	+ 0.5	- 20	- 18	- 10
6 (comparison)	0	+ 0.3	- 10	- 12	- 10
7 (comparison)	0	0	- 2	- 11	- 10
8 (comparison)	0	- 0.6	- 10	- 9	- 11
9 (invention)	0	+ 0.8	- 12	- 15	- 7
10 (invention)	0	+ 1.0	- 15	- 14	- 9

Tables 2 and 3 show that samples 2-4, containing potassium bromide but no additional stabilizing compound, give a speed increase and small contrast decreases on the fresh coated materials versus reference sample 1, but the decrease of contrast values is still unacceptable after the samples have been subjected to the incubation test. In fact, the contrast values are considered acceptable in the present invention when the variation is lower than 15%. Samples 5-8, containing Compound (1) of the present invention but not containing potassium bromide, have too low shoulder contrast (lower than 11.0) and speed on the fresh materials, even if the keeping properties are good. Samples 9 and 10, containing both potassium bromide and Compound (1) of the present invention, give good speed and contrast values on the fresh coated materials; said sensitometric properties are very good also after the incubation test, with a small increase in the variation of the speed and a low variation of the contrast values, much lower than those of reference sample 1.

EXAMPLE 2

Sample 11 was prepared as Sample 10 of Example 1, but the amount of Compound (1) was of 0.13 mmoles per silver mole.

Sample 12 was prepared as Sample 11, but Compound (1) of the present invention was replaced by Compound (2) of the present invention.

Sample 13 was prepared as Sample 11, but Compound (1) of the present invention was replaced by 0.50 mmoles per silver mole of the Compound (5) of the present invention.

Sample 14 was prepared as Sample 11, but Compound (1) of the present invention was replaced by 0.50 mmoles per silver mole of the compound (6) of the present invention.

Sample 15 was prepared as Sample 11, but Compound (1) of the present invention was replaced by comparison Compound A.

Sample 16 was prepared as Sample 11, but Compound (1) of the present invention was replaced by comparison Compound B.

Sample 17 was prepared as Sample 11, but Compound (1) of the present invention was replaced by comparison Compound C.

Sample 18 was prepared as Sample 11, but Compound (1) of the present invention was replaced by comparison Compound D.

Sample 19 was prepared as Sample 11, but Compound (1) of the present invention was replaced by comparison Compound E.

Sample 20 was prepared as Sample 11, but Compound (1) of the present invention was replaced by 0.50 mmoles per silver mole of comparison Compound E.

The samples were evaluated after exposure as described in Example 1. Table 4 shows the sensitometric results obtained on fresh coated materials; Table 5 shows the percentage of variation of said sensitometric values obtained after incubation test (5 days at 50% RH, at 60°C).

Table 4

Samples	Dmin	Sensitivity	Toe Contrast	Average Contrast	Shoulder Contrast
11 (invention)	0.03	3.43	1.08	9.04	12.8
12 (invention)	0.03	3.44	1.17	8.90	12.4
13 (invention)	0.03	3.49	1.12	9.20	14.2
14 (invention)	0.03	3.49	1.15	9.20	13.4
15 (comparison)	0.03	3.43	1.17	8.95	12.9
16 (comparison)	0.03	3.45	1.23	9.10	12.8
17 (comparison)	0.03	3.44	1.19	8.80	12.4
18 (comparison)	0.03	3.44	1.18	8.80	12.8
19 (comparison)	0.03	3.44	1.19	8.95	12.6
20 (comparison)	0.04	3.45	1.22	8.86	12.7

Table 5

Samples	% Dmin	% Sensitivity	% Toe Contrast	% Average Contrast	% Shoulder Contrast
11 (invention)	0	+ 0.3	+ 2	- 12	- 14
12 (invention)	0	+ 0.9	- 3	- 11	- 8
13 (invention)	0	+ 0.3	- 14	- 4	2
14 (invention)	0	+ 0.3	- 8	- 4	- 1
15 (comparison)	0	+ 2.0	- 19	- 15	- 8
16 (comparison)	0	+ 1.1	- 25	- 18	- 11
17 (comparison)	+ 33	+ 2.0	- 15	- 16	- 10
18 (comparison)	0	+ 2.0	- 19	- 16	- 14
19 (comparison)	+ 33	+ 1.7	- 4	- 13	- 10
20 (comparison)	+ 33	+ 1.3	- 16	- 13	- 13

Table 4 shows that all fresh coated samples have good sensitometric properties, but, as shown in Table 5, only Samples 11 to 14 of the present invention had a very little variation in said sensitometric values obtained on incubation test.

EXAMPLE 3

Sample 21 was prepared as Sample 11 of Example 2, but the potassium bromide salt was added after the addition of the spectral sensitizing dye, rather than before as in Sample 11.

Sample 22 was prepared as Sample 11 without the addition of Compound (1).

Sample 23 was prepared as Sample 22, but the potassium bromide salt was added after the addition of the spectral sensitizing dye, rather than before as in Sample 22.

The samples were evaluated after exposure as described in Example 1. Table 6 shows the sensitometric results obtained on fresh coated materials; Table 7 shows the percentage of variation of said sensitometric values obtained after incubation test (5 days at 50% RH, 60°C).

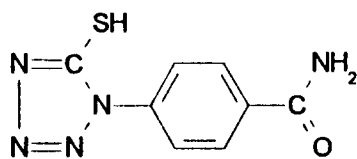
Table 6

Samples	Dmin	Sensitivity	Toe Contrast	Average Contrast	Shoulder Contrast
11 (invention)	0.03	3.43	1.08	9.04	12.8
21 (comparison)	0.03	3.39	0.97	9.20	12.2
22 (comparison)	0.03	3.45	1.25	9.01	13.2
23 (comparison)	0.03	3.49	1.39	9.29	14.0

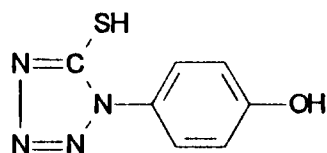
Table 7

Samples	% Dmin	% Sensitivity	% Toe Contrast	% Average Contrast	% Shoulder Contrast
11 (invention)	0	+ 0.3	+ 2	- 12	- 14
21 (comparison)	+ 33	+ 3.2	+ 10	- 22	- 10
22 (comparison)	0	+ 1.7	- 25	- 21	- 17
23 (comparison)	+ 33	+ 2.0	- 32	- 21	- 21

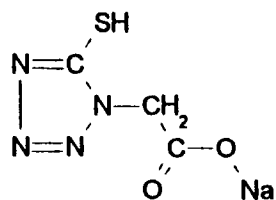
Table 6 shows that comparison Sample 21, obtained with potassium bromide added after the spectral sensitizing dye, has a lower speed on the fresh material and very large variation of sensitometric values on incubation test, while Sample 11, identical to Sample 21 but obtained with potassium bromide added before the spectral sensitizing dye, shows very good keeping properties.



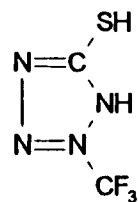
(Comparison Compound A)



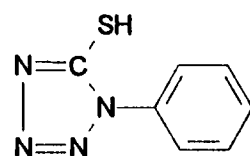
(Comparison Compound B)



(Comparison Compound C)



(Comparison Compound D)



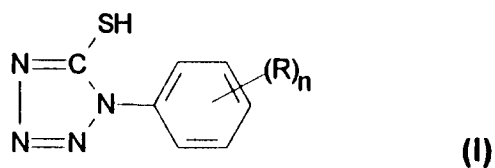
(Comparison Compound E)

Claims

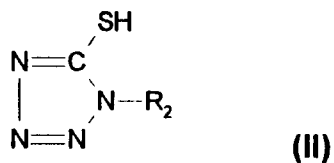
1. Method for stabilizing a photosensitive silver halide emulsion which comprises the following steps, in sequence:

- a) adding to said emulsion a water-soluble bromide salt;
- b) spectrally sensitizing said emulsion;

c) adding to said spectrally sensitized emulsion a compound having the following formula (I):

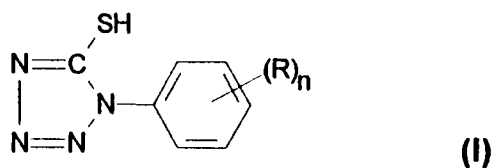


10 wherein R represents nitro, cyano, fluoroalkyl, halogen, $-\text{COOR}_1$ group, R_1 being hydrogen or an alkyl group, and n is an integer from 1 to 5; or having the following formula (II):



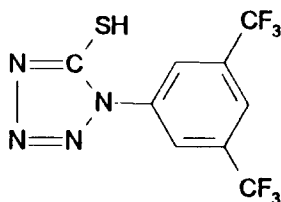
20 wherein R_2 is a branched alkyl chain having from 3 to 5 carbon atoms.

- 25
2. Method for stabilizing a photosensitive silver halide emulsion of claim 1, wherein the water-soluble bromide salt is ammonium bromide or potassium bromide.
 3. Method for stabilizing a photosensitive silver halide emulsion of claim 1, wherein said compound has the following formula:

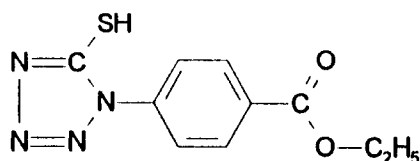


wherein R represents fluoroalkyl, and n is an integer from 1 to 5.

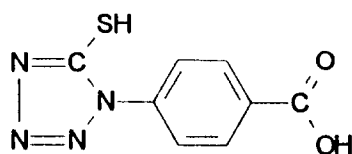
- 40
4. Method for stabilizing a photosensitive silver halide emulsion of claim 1, wherein said compound has the following formula :



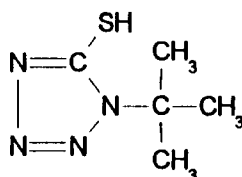
5. Method for stabilizing a photosensitive silver halide emulsion of claim 1, wherein said compound has the following formula:



6. Method for stabilizing a photosensitive silver halide emulsion of claim 1, wherein said compound has the following formula:



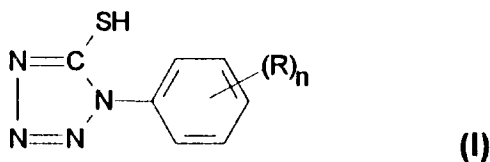
7. Method for stabilizing a photosensitive silver halide emulsion of claim 1, wherein said compound has the following formula:



8. Method for stabilizing a photosensitive silver halide emulsion of claim 1, wherein said emulsion is spectrally sensitized with a sensitizing dye suitable for exposure in the range from about 620 nm to about 680 nm.

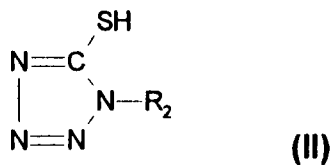
9. Method for stabilizing a photosensitive silver halide emulsion of claim 1, wherein said emulsion is doped with iridium, ruthenium and/or rhodium dopants.

10. Light-sensitive silver halide photographic element comprising a support bearing at least one light-sensitive silver halide emulsion layer comprising a water-soluble bromide salt and a compound having the following formula (I):



wherein R represents nitro, cyano, fluoroalkyl, halogen, -COOR₁ group, R₁ being hydrogen or an alkyl group, and

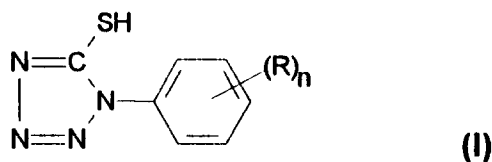
n is an integer from 1 to 5; or having the following formula (II):



wherein R_2 is a branched alkyl chain having from 3 to 5 carbon atoms.

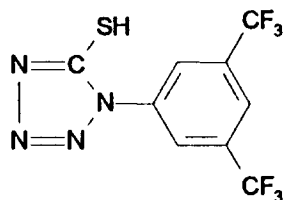
11. Light-sensitive silver halide photographic element of claim 10, wherein the water-soluble bromide salt is ammonium bromide or potassium bromide.

12. Light-sensitive silver halide photographic element of claim 10, wherein said compound has the following formula :

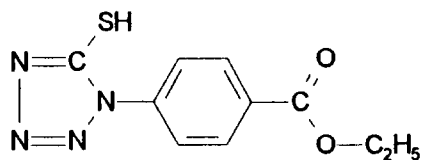


wherein R represents fluoroalkyl, and **n** is an integer from 1 to 5.

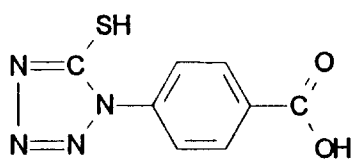
13. Light-sensitive silver halide photographic element of claim 10, wherein said compound has the following formula :



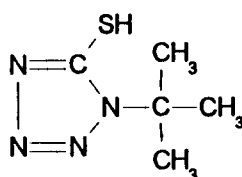
14. Light-sensitive silver halide photographic element of claim 10, wherein said compound has the following formula :



15. Light-sensitive silver halide photographic element of claim 10, wherein said compound has the following formula :



16. Light-sensitive silver halide photographic element of claim 10, wherein said compound has the following formula :



17. Light-sensitive silver halide photographic element of claim 10, wherein said emulsion is spectrally sensitized with a sensitizing dye suitable for exposure in the range from about 620 nm to about 680 nm.

18. Light-sensitive silver halide photographic element of claim 10, wherein said emulsion is doped with iridium, ruthenium and/or rhodium dopants.

19. Light-sensitive silver halide photographic element of claim 10, wherein said emulsion is a chlorobromide emulsion having a chloride content of at least 50% moles.

20. Light-sensitive silver halide photographic element of claim 10, wherein said emulsion has an average grain size equal or lower than 0.30 μm .

21. Light-sensitive silver halide photographic element of claim 10, wherein the amount of said compound is in the range from about 0.05 to about 2.0 millimoles per silver mole.

22. Light-sensitive silver halide photographic element of claim 10, wherein the amount of said compound is in the range from about 0.20 to about 1.70 millimoles per silver mole.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 11 4617

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
D,Y	US-A-4 332 888 (L. D. CORBEN) 1 June 1982 * column 2, line 34 - column 4, line 3 * ---	1-22	G03C1/005 G03C1/34
A	EP-A-0 600 308 (MINNESOTA MINING AND MANUFACTURING COMPANY) 8 June 1994 * page 3, line 56 - page 6, line 45 * ---	1-22	
D,A	US-A-4 830 958 (M. OKUMURA ET AL.) 16 May 1989 * column 1, line 11 - column 1, line 16 * * column 10, line 57 - column 19, line 28 * * * examples 1-3 * ---	1-22	
X,Y	EP-A-0 440 947 (MINNESOTA MINING AND MANUFACTURING COMPANY) 14 August 1991 * page 2, line 3 - page 2, line 8 * * page 3, line 17 - page 4, line 44 * * examples 1-4 * -----	1-22	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			G03C
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 8 December 1995	Examiner Markowski, V
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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