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EUROPEAN PATENT SPECIFICATION

45 Date of publication of patent specification: **15.05.85**

51 Int. Cl.⁴: **G 03 C 1/40**, **G 03 C 1/28**,
G 03 C 1/34, **G 03 C 1/02**

21 Application number: **81901016.6**

22 Date of filing: **02.10.80**

80 International application number:
PCT/US80/01402

87 International publication number:
WO 82/01260 15.04.82 Gazette 82/10

54 **CHEMICALLY SENSITIZED SILVER HALIDE PHOTOGRAPHIC EMULSIONS AND COLOR PHOTOGRAPHIC ELEMENTS CONTAINING SAID EMULSIONS.**

43 Date of publication of application:
06.10.82 Bulletin 82/40

45 Publication of the grant of the patent:
15.05.85 Bulletin 85/20

84 Designated Contracting States:
DE FR GB

50 References cited:
US-A-1 678 832
US-A-3 434 842
US-A-3 753 908
US-A-3 859 100
US-A-4 116 697

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Courier Press, Leamington Spa, England.

Description**Field Of The Invention**

The present invention relates to the use of certain compounds useful as sulfur sensitizers for silver halide photographic emulsions associated with color couplers for use in color photography.

More particularly, the present invention refers to silver halide photographic emulsions associated with color couplers sensitized with a particular class of sulfur sensitizer compounds and to photographic elements containing said emulsions.

Background Of The Art

Silver halide photographic emulsions are generally prepared by precipitating small silver halide crystals in the presence of a protective colloid, e.g. gelatin. The crystals obtained upon precipitation are grown to the required grain size (ripened) by heating them for a given period of time in the presence of a silver halide solvent. The so prepared photographic emulsion inherently has a rather low light sensitivity. In order to increase its sensitivity, the ripened emulsion is reacted with chemical sensitizers, i.e. with compounds capable of forming sensitivity centers on the grains. Compounds capable of forming sensitivity centers are usually characterized by the presence of one or more sulfur atoms, capable of forming complexes with the silver halide which can decompose into silver sulfide. This sulfiding operation is called chemical digestion, and typical sulfur sensitizers, which can be present in gelatin as impurities or can be deliberately added to the emulsion, are for instance thiosulfate, allylthiourea, thiourea and 2-thio-succinimide. When the maximum sensitivity has been achieved with these compounds, a further increase can be obtained upon gold sensitization, e.g. upon addition of small quantities of complex gold salts, such as ammonium gold thiocyanate.

The sensitivity center formation, in addition to the sensitivity increase, involves also other changes in the photographic properties of the emulsion, among which the most serious is fog. This phenomenon occurs in a certain percentage of crystals which are developable without exposure to light. During chemical digestion, sensitivity centers are prevalently formed, but at the same time fog centers are also formed.

Generally, sensitivity reaches an optimal value at a given digestion time; once that this time has been exceeded, sensitivity starts decreasing while fog density continues to increase.

In some cases, particularly when the emulsions are for materials which are to be processed by high-temperature rapid processing, during the chemical digestion of the emulsion for instance with thiosulfate, a fog increase is caused even before the emulsion reaches the flat portion of the ripening curve and therefore before the desired reactivity is reached. To reach the required reactivity in these cases, chemical digestion is performed until the required sensitivity is obtained, and fog is reduced and controlled by means of antifoggants, i.e. substances which should have the property of decreasing fog more than sensitivity. Unfortunately, these substances have the drawback of also reducing to a certain extent the sensitivity and the reactivity of the sensitive layer. Additionally, such antifoggants, being adsorbed by the silver halide crystals, may interfere with the other operations which are important in the photographic layer.

In the case of color photographic materials, these emulsions are associated with nondiffusing couplers which in the presence of exposed silver halide are capable of reacting with p-phenylene diamine developers to form a dye image-wise distributed in the developed photographic element.

Such non-diffusing couplers can be introduced into the photographic layer containing them (generally the silver halide emulsion layer or a layer adjacent thereto) either in an aqueous alkaline solution (in this case at least an acid solubilizing group of the SO_3H or COOH type must be introduced into the coupler molecule itself), or dissolved in a high-boiling solvent dispersed in the coating composition of the layer itself.

Briefly, this second method, which at present is the preferred one, is called "dispersion method" and substantially consists of first dissolving the coupler in a substantially water-immiscible organic solvent and then dispersing the so-obtained solution as extremely tiny droplets into a hydrophilic colloidal binder. Gelatin is the preferred hydrophilic colloidal binder, but other known polymeric colloidal binders can also be used. (A description of the dispersion method can be found in U.S. Patents 2,322,027; 2,801,170; 2,801,171 and 2,991,177).

U.S. Patent 3,859,100 discloses the use of at least one triazaindene, tetraazaindene or pentaazaindene having at least one hydroxy group and at least one compound having a 1,2-dithiolane or a 1,2-dithiane ring to reduce fog without a reduction in desirable photographic characteristics.

In this particular type of color photography, including couplers associated with silver halide emulsions, the problem of fog associated with the high reactivities of the materials is particularly delicate since the product can hardly tolerate fog values even only slightly higher than the natural minimum ones (which substantially correspond to the supporting base fog) while at the same time the reactivity of the exposed emulsions associated with the couplers tends to be difficult to control during the color development with p-phenylene diamine developer.

Accordingly, it is desired to increase the sensitivity and reactivity of silver halide photographic emulsions associated with color couplers for use in color photography to obtain dye images.

In particular, it is desirable to obtain silver halide photographic emulsions associated with color couplers with an optimal sensitivity/fog ratio.

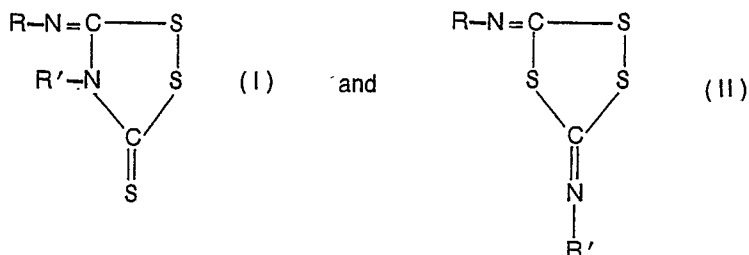
More particularly, it is desirable to obtain silver halide photographic emulsions associated with color couplers having a good fog kinetics, without the need of excessive quantities of antifoggant agents.

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Summary Of The Invention

According to the present invention new agents are provided for chemically sensitizing the silver halide emulsion associated with color couplers, which agents have the following formulas:

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or mixtures thereof,

wherein R is a hydrogen atom, aliphatic group or an aromatic or non-aromatic cyclic nucleus and R' is a hydrogen atom, an aliphatic group or an aromatic or non-aromatic cyclic nucleus, at least one of them being different from hydrogen.

A preferred aromatic nucleus is a phenyl group unsubstituted or substituted with an alkyl or an alkoxy group having no more than 4 carbon atoms or with a halogen substituent, preferably chlorine, as for example, phenyl, p-methoxy-phenyl, p-chloro-phenyl. A preferred cyclic non aromatic nucleus (saturated or not saturated) is a cyclohexyl or cyclohexenyl group.

More preferably, R and R' are both alkyl groups having from 1 to 4 carbon atoms, and most preferably they are methyl groups.

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Detailed Description of The Invention

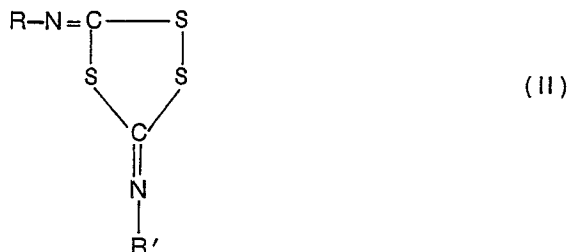
Accordingly, the present invention refers to a silver halide photographic emulsion associated with color couplers for the use in photography to obtain dye images and containing a sensitizing amount of sulfur sensitizer characterized in that the sulphur sensitizer is a 1,2,4-dithiazolidino-3-thione sulfur sensitizer corresponding to the formula:

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or a dimethylenetrisulfide sulfur sensitizer corresponding to the formula:



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or mixture thereof,

wherein R is an aliphatic chain, preferably having no more than 4 carbon atoms, or a cyclic aromatic or non-aromatic nucleus, preferably a 5 or 6 membered nucleus, at least R or R' being different from hydrogen.

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More preferably, the present invention refers to a photographic emulsion, as described above, wherein both R and R' are methyl groups.

More preferably, the present invention refers to a photographic emulsion, as described above, containing also a sensitizing amount of a noble metal salt, such as a gold sensitizer.

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The present invention further refers to a photographic element including a supporting base and a silver

halide emulsion associated with a coupler and containing a sensitizing amount of a sulfur sensitizer, characterized in that the sulfur sensitizer is as described above.

The present invention in a further aspect refers to a method for manufacturing a silver halide photographic emulsion for use in color photography which includes the addition of at least one sulfur sensitizing compound, characterized in that the sulfur sensitizing compound is as hereinbefore defined and that the defined sulfur sensitizing compound can be added to the silver halide emulsion prior to or during the chemical digestion and the subsequent addition of a color coupler prior to the coating of the obtained photographic composition.

In fact, we have found that it is possible to sensitize a silver halide photographic emulsion associated with color couplers by adding at least one sulfur sensitizer of the present invention to an emulsion prior to or during the chemical digestion.

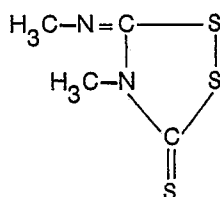
We have further found that better fog kinetics and higher reactivity are obtained with the sulfur sensitizers of the present invention rather than with the conventional sulfur sensitizers, without having to add high quantities of stabilizers and antifoggants at the end of the digestion.

Some experiments have shown that the optimal quantity of sulfur sensitizer used in the present invention depends upon the specific compound which is used, upon the nature of the colloidal binding agent for the silver halide crystals, upon the quantity, type and size of the silver halide crystals, upon the digestion time and temperature and upon the emulsion pH and pAg-values. We have found they can be used in a quantity ranging from 0.001 to 0.25 millimoles, preferably from 0.01 to 0.1 millimoles, per mole of silver.

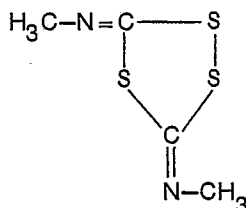
In particular, we have found that the new sulfur sensitizers of the present invention can be used in combination with other sensitizers known in the art, such as e.g. gold salts. We have found that it is possible to restrain fog formation, which is normally caused by combining the conventional sulfur sensitizers during the chemical digestion, by employing the new sulfur sensitizers of the present invention in combination with gold sensitizers even without using excessive and harmful quantities of stabilizers and antifoggants.

The following compounds fall within classes I and II of the sulfur sensitizers of the present invention and are significant examples thereof:

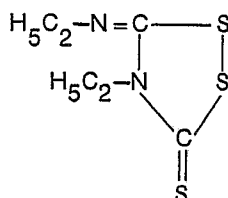
1) 4-methyl-5-methylimino-1,2,4-dithiazolidine-3-thione



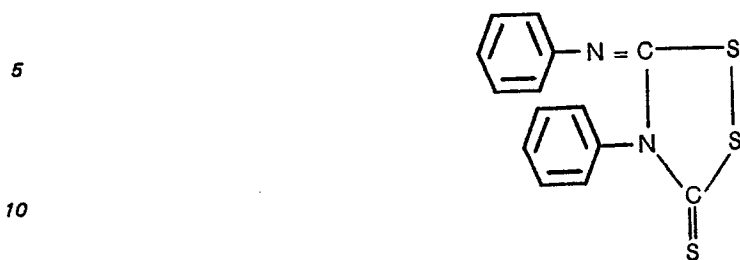
2) 2,5-dimethylimino-dimethylentrisulfide



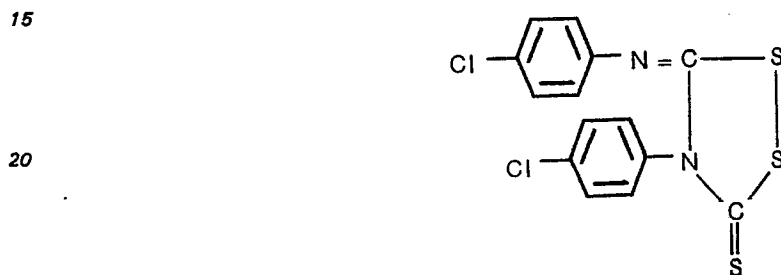
3) 4-ethyl-5-ethylimino-1,2,4-dithiazolidine-3-thione



4) 4-phenyl-5-phenylimino-1,2,4-dithiazolidine-3-thione



5) 4-(4'-chloro)-phenyl-5-(4' chloro)-phenylimino-1,2,4-dithiazolidine-3-thione



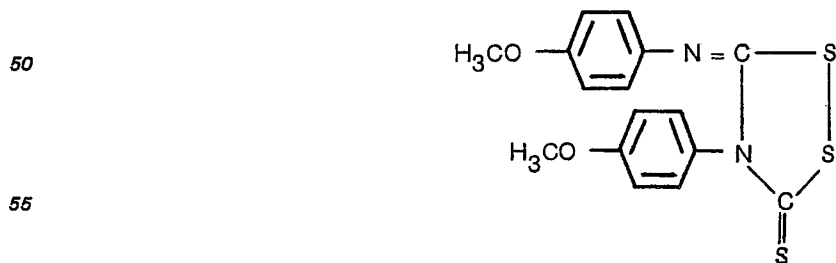
6) 5-acetylimino-1,2,4-dithiazolidine-3-thione



7) 5-propionylimino-1,2,4-dithiazolidine-3-thione



8) 4-(4'-methoxy)-phenyl-5-(4'-methoxy)-phenylimino-1,2,4-dithiazolidine-3-thione



Some experiments have shown that both compound classes (I) and (II), at least in some cases, can be in an isomeric equilibrium in an alkaline water solution (a reference to such equilibrium is described by N. Khavasch and C. Mayer in "The Chemistry of Sulfur Compounds", Pergamon Press (1966), 273 and by W. Schmiedt, Annalen der Chemie, 635 (1960), 109). Preparation example 2, reported hereinafter, is a specific case of this equilibrium since it shows the possibility of preparing a dimethyltrisulfide upon basic treatment of a 1,2,4-dithiazolidine-3-one.

All these compounds were prepared according to descriptions in the literature and more precisely by

M. Freund and E. A. Ashbrand in *Annalen der Chemie*, 285 (1894), 166—203 and in *Berichte*, 9, (1876), 1262; the synthesis thereof is described with details in the following preparative examples.

Example 1

5 4-methyl-5-methylimino-1,2,4-dithiazolidine-3-thione (Compound 1)



15 A mixture of 50.0 g of methylamine (50% water solution) and 40.0 g of carbon disulfide was cooled with an ice bath and stirred. 50 ml of ethanol were added dropwise by keeping the temperature under 40°C. At the end of the addition, the mixture obtained was stirred 15 minutes at room temperature and then treated with 40.0 g of bromine dissolved in 100 ml of chloroform, maintaining the reaction temperature between 6 and 10°C. The reaction solution was stirred two more hours at 10—15°C and cooled. The raw
20 solid product obtained was collected on a Buchner and washed with 50 ml of chloroform. The product was cool treated with 60 ml of Na₂CO₃ (10% water solution) for one hour, filtered and washed again with water. After a crystallization from ethanol, 5 g of pure product were obtained having a M.P. = 82—84°C.

Percent analysis:

	Calculated	Found
25 C%	26.93	26.43
H%	3.39	3.34
N%	15.71	15.44

Example 2

30 2,5-dimethylimino-dimethylentrisulfide (Compound 2)



2.5 g of compound 1 were treated to reflux temperature for one hour with a solution formed by 90 ml of ethanol and 10 ml of diluted ammonia (30% water solution). After cooling overnight, the solid product was collected on a Buchner and purified by crystallization from absolute ethanol. 0.5 g of pure product were
45 obtained having a M.P. = 114—116°C.

Example 3

50 4-ethyl-5-ethylimino-1,2,4-dithiazolidine-3-thione (Compound 3)



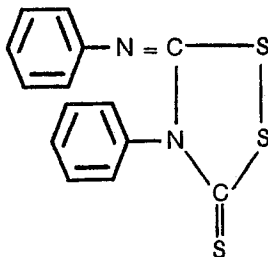
A mixture of 30 g of ethylisothiocyanate and 100 ml of chloroform was placed in a 250 ml flask equipped with reflux condenser, mechanical stirrer and dropping funnel. To this were added dropwise
60 18.5 g of bromine dissolved in 50 ml of chloroform. During the addition the temperature was kept around 30—40°C and a yellow product separated out from the solution. This product was dissolved at 60°C in 220 ml of deionized water and the obtained solution was cooled overnight. The white product obtained was treated with an aqueous solution of Na₂CO₃ at pH = 9 by cooling: a yellow oil was obtained. The oil was extracted with ethyl ether, dried with anhydrous sodium sulfate and the solvent distilled off. The oil
65 obtained was used without further purification.

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Percent analysis:	Calculated	Found
N%	13.58	13.01

Example 4

4-phenyl-5-phenylimino-1,2,4-dithiazolidine-3-thione (Compound 4)

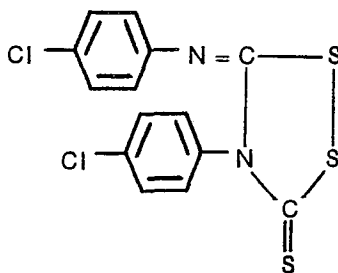


A mixture of 40.56 g of phenylisothiocyanate and 100 ml of chloroform was placed in a 500 ml flask equipped with reflux condenser, thermometer, mechanical stirrer and drop-in funnel. To this was added dropwise a solution formed by 16 g of bromine and 30 ml of chloroform. During the addition the temperature was kept around 25°C and at the end of the reaction the mixture was stirred for 6 hours at room temperature and then cooled overnight. The orange solid product obtained was boiled with 140 ml of absolute ethanol for one hour and then cooled. The yellow raw product obtained was crystallized from absolute ethanol, obtained 4 g of pure product having a M.P. = 150°C.

Percent analysis:	Calculated	Found
C%	55.60	55.55
H%	3.33	3.30
N%	9.26	9.30

Example 5

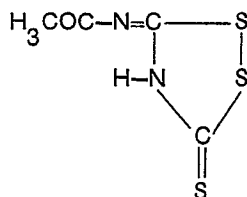
4-(4'-chloro)-phenyl-5-(4'-chloro)-phenylimino-1,2,4-dithiazolidine-3-thione (Compound 5)



This product was prepared according to example 4, using 4-chloro-phenyl-isothiocyanate and ligroin as solvent.

Example 6

5-acetylimino-1,2,4-dithiazolidine-3-thione (Compound 6)



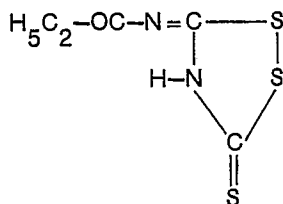
This compound was prepared according to Berichte 6 (1873) 902 and in Annalen der Chemie 331 (1904), 296, by reacting ammonium isothiocyanate (135 g) and acetic anhydride (90 ml) at 74—76°C for two hours and a half. The raw product separated on cooling was collected on a Buchner funnel and washed

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repeatedly with deionized water. After recrystallization from toluolated ethanol, 10 g of pure product were obtained.

Percent analysis:	Calculated	Found
C%	24.99	25.36
H%	2.19	2.10
N%	14.57	14.96

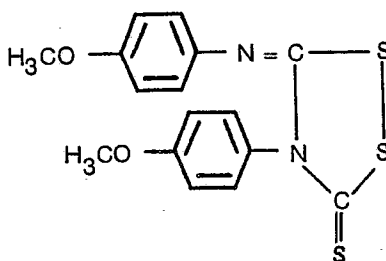
Example 7 5-propionylimino-1,2,4-dithiazolidine-3-thione (Compound 7)



This compound was prepared according to example 6, using propionic anhydride instead of acetic anhydride.

Percent analysis:	Calculated	Found
C%	29.11	29.09
H%	2.93	3.07
N%	13.58	13.78

Example 8 4-(4'-methoxy)-phenyl-5-(4'-methoxy)-phenylimino-1,2,4-dithiazolidine-3-thione (Compound 8)



This compound was prepared according to example 1, using 4-methoxy-phenyl-isothiocyanate instead of phenylisothiocyanate.

The silver halide emulsion type, which can be chemically digested according to the present invention is not critical. Thus, the emulsion can be a silver chloride, a silver iodide, a silver chloro-bromide, a silver chloro-iodide, a silver bromo-iodide, or a silver chlorobromo-iodide emulsion. The preparation and the types of emulsions which can be used for the present invention are for instance those described in research Disclosure, vol. 176, December 1978, item 17643 I. The silver halide emulsions can be unwashed or washed to remove the soluble salts, as for instance described in Research Disclosure, vol. 176, December 1978, item 17643 II. The silver halide emulsions, further to the sulfur sensitizers of the present invention, can be also chemically sensitized with active gelatins, noble metal salts or with reducing substances, as described in Research Disclosure, vol. 176, December 1978, item 17643 III. The silver halide emulsions can be spectrally sensitized with dyes of various classes, among which there is the polymethine dye class, which includes cyanines, merocyanines, complex cyanines and merocyanines, oxonoles, hemioxonoles, styryls, merostyryls, and streptocyanines, as described in Research Disclosure, vol. 176, December 1978, item 17643 IV. Optical brighteners can be employed in the photographic element which include said emulsions, as those described in Research Disclosure, vol. 176, December 1978, item 17643 V. The instability which increases the minimum density (i.g. fog) in negative-type emulsion coatings or which decreases the maximum density in direct-positive emulsion coatings, can be avoided by adding stabilizers, antifoggants, antikinking agents, latent-image stabilizers and the like to the emulsions and adjacent layers prior to coating, as described in Research Disclosure, vol. 176, December 1978, item 17643 VI. The dye forming

couplers, which are to be associated with the photographic emulsion of the present invention, are chosen to form subtractive primary (i.e. yellow, magenta and cyan) image dyes and are non-diffusible, colorless couplers, such as two and four-equivalent couplers of the open-chain ketomethylene, pyrazolone, phenol and naphthol type. Such couplers are for example described in Research Disclosure, vol. 176, December 1978, item 17643 VII D and E. The photographic element can incorporate colored dye forming couplers, such as those employed to form integral masks for negative color images, as illustrated in Research Disclosure, vol. 176, December 1978, item 17643 VII G. The dye forming couplers can release upon coupling photographically useful fragments, such as development inhibitors or accelerators, bleach accelerators, hardeners and so on, as described in Research Disclosure, vol. 176, December 1978, item 17643 VII F. The above dye forming couplers can be incorporated in the photographic element, as described in Research Disclosure, vol. 176, December 1978, item 17643 VII C. Incident and reflected radiation can be absorbed or scattered by incorporating materials for that purpose in the photographic element layers. Reflective or absorbing materials incorporated directly in the silver halide emulsion layers can increase speed or sharpness. Filter materials, typically located in overcoat and interlayers, can trim spectrally or attenuate incident radiation and antihalation materials, typically located in undercoat and backing layers, can eliminate or diminish reflection (halation) exposure of emulsion layers. Reflective and absorbing materials are for instance those described in Research Disclosure, vol. 176, December 1978, item 17643 VIII; Photographic silver halide emulsion layers and other layers on photographic elements can contain various colloids alone or in combination as vehicles, as described for instance in Research Disclosure, vol. 176, December 1978, item 17643 IX. The layers of the photographic element containing cross-linkable colloids, particularly the gelatin-containing layers, can be hardened by various organic and inorganic hardeners, as those described in Research Disclosure, vol. 176, December 1978, item 17643 X. The photographic element layers can contain various types of coating aids, such as anionic, cationic, non-ionic or zwitterionic surfactants, alone or in combination, as those described in Research Disclosure, vol. 176, December 1978, item 17643 XI. The flexibility of the photographic element layers upon drying can be improved through the incorporation of plasticizers, as described in Research Disclosure, vol. 176, December 1978, item 17643 XII A. The photographic element can contain lubricants to reduce sliding friction encountered in use, as described in Research Disclosure, vol. 176, December 1978, item XII B. The photographic element can contain conducting layers, such as antistatic layers, as described in Research Disclosure, vol. 176, December 1978, item 17643 XIII. The sensitizing dyes and the other addenda incorporated into the layers of the photographic element can be dissolved and added prior to coating either from water or organic solvent solutions, by following various techniques as described in Research Disclosure, vol. 176, December 1978, item 17643 XIV. In forming the photographic element the layers can be located on the photographic element the layers can be located on the photographic support by various procedures, as described in Research Disclosure, vol. 176, December 1978, item 17643 XV A. The coated layers of the photographic element can be dried by various procedures, as described in Research Disclosure, vol. 176, December 1978, item XV B. The layers of the photographic element can contain matter agents, as for instance described in Research Disclosure, vol. 176, December 1978, item 17643 XVI. The layers of the photographic element can be coated on a variety of supports provided with one or more layers to enhance the adhesive, antistatic dimensional, abrasive, hardness, frictional, antihalation and/or other properties, as described in Research Disclosure, vol. 176, item 17643 XVII. The light sensitive silver halide contained in the photographic element can be processed following exposure to form a visible image by associating the silver halide with an aqueous alkaline medium in the presence of a developing agent contained in the medium or element with a variety of formulations and techniques, as described in Research Disclosure, vol. 176, December 1978, item 17643 XIX.

The invention is now illustrated by the following procedures and examples.

PROCEDURE A

A gelatin silver halide emulsion containing 91% mole silver bromide, 7.8% mole silver chloride and 1.2% mole silver iodide was prepared in the usual way by adding AgNO_3 solution to the alkaline halide solution and after physical digestion it was coagulated by means of carbamoyl gelatin. The coagulum was redispersed in a gelatin solution at 65°C at a silver-to-gelatin ratio of 0.30. The emulsion thus obtained was ripened at $\text{pAg} = 7.9$ and $\text{pH} = 5.5$ by adding 15 μ -moles of AuCl_3 and 950 μ -moles of KSCN as complex solution and 44 μ -moles of $\text{Na}_2\text{S}_2\text{O}_3$ per mole of silver. Three samples of the emulsion were then digested at 47°C for three different times respectively, i.e. A = 100', B = 150', C = 200'. To these emulsion samples were then added the following antifoggants: 50 mg/Ag mole of hexahydro-1-phenyl-4,6-diimino-1, 3-pyrimidine-2-thione and 40 mg/Ag mole of phenylmercaptobenzimidazole, then with coating aids, gelatin hardeners and yellow coupler α - pivalyl - α - (3 - chloro - 1,2,4 - triazolyl) - 5 - [α - (2,4 - ditert. - amylphenoxy) - butyramido] - 2 - chloro - acetanilide dispersion, and coated on a triacetate base (14/100) with a silver covering weight of 1.05 g Ag/m². A protective gelatin layer was coated onto. The strips obtained were exposed in a sensitometer and processed in a standard Kodak ECP 2 processing line for color positive films. The developed strips were evaluated with a computerized densitometer.

PROCEDURE B

A gelatin silver chloro-bromide emulsion containing 72% mole silver chloride and 28% mole silver

bromide was prepared in the usual way and coagulated by means of carbamoyl gelatin. The coagulum was redispersed in gelatin solution at 57°C with a silver-to-gelatin ratio of 0.38. The emulsion thus obtained was ripened at pAg = 7.3 and pH = 5.5 by adding 34 μ -moles of AuCl₃ and 53 μ -moles of Na₂S₂O₃ per mole of silver. Three different ripening tests were made at 55°C for three times respectively, i.e. A = 100', B = 150' and C = 200'. These emulsion samples were added with stabilizers, coating aids, gelatin hardeners and magenta coupler 1 - (6 - chloro - 2,4 - dimethylphenyl) - 3 - [α - (m - penta-decylphenoxy) - butyramido] - 5 - pyrazolone dispersion and coated on a triacetate base (14/100) with a silver covering weight of 0.80 g/m². A protective gelatin layer was coated onto. The strips obtained were exposed and processed in a standard Kodak ECP 2 processing line for color positive materials. The processed films were evaluated with a computerized densitometer.

PROCEDURE C

A gelatin silver halide emulsion containing 85% mole silver bromide, 14% mole silver chloride and 1% mole silver iodide has been prepared by the double jet technique and then coagulated by means of carbamoyl gelatin. The emulsion thus obtained was digested at pAg = 7.9 and pH = 5.5 with 14 μ -moles Au per silver mole and 44 μ -mole thiosulfate per silver mole for three different times, i.e. A = 100', B = 150' and C = 200' at 46°C. The digested emulsion samples were added with the coating aids, yellow coupler α - pivalyl - α - (3 - chloro - 1,2,4 - triazolyl) - 5 - [α - (2,4 - ditert. - amylphenoxy) - butyramido] - 2 - chloro - acetanilide dispersion and coated on a triacetate base with a silver covering weight of 0.80 g/m². The antifog quantity added before coating was at a lower level than the normal quantity necessary to get standard keeping properties.

PROCEDURE D

A gelatin silver chloro-bromide emulsion was made substantially as described in Procedure B. The emulsion thus obtained was digested by adding 30 μ -mole thiosulfate per silver mole and adjusting the pH at 5.5 and pAg 7.3. The digestion was made at three different times, i.e. A = 100', B = 150' and C = 200' at 55°C. The emulsion samples, thus obtained, were coated as described in Procedure B.

Example 9

A gelatin silver halide emulsion was prepared as described in Procedure A. Three other samples of the redispersed emulsion were added with an equimolar solution quantity of Compound 4, instead of the thiosulfate solution. They were digested and coated as described before. The results are shown in Table 1.

TABLE 1

Sensitizer	μ M/Ag mole	Ripening time at 47°C (minutes)	Fog (1)	Speed (2)	Y_M (3)
Na ₂ S ₂ O ₃	49	100	1.11	—	—
"	"	150	2.31	—	—
"	"	200	2.70	—	—
Compound 4	49	100	0.13	1.05	4.19
"	"	150	0.20	1.04	3.89
"	"	200	0.62	0.95	2.67
Na ₂ S ₂ O ₃ (°)	49	140	0.14	1.16	3.81

(°) Prepared as described in Procedure A, but containing 100 mg/Ag mole of hexahydro-1-phenyl-4,6-diimino-1,3-pyrimidine-2-thione plus 80 mg/Ag mole of phenylmercaptobenzimidazole plus 10 g/Ag mole of sodium toluensulfinate antifoggants and stabilizers.

(1) Fog = D.min.

(2) Speed = sensitivity expressed in log It measured at D=1.

(3) Y_M = medium contrast measured between the points D=0.9 and 2.10.

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Example 10

A gelatin silver chloro-bromide emulsion has been prepared as described in Procedure B; three samples of the redispersed emulsion have been added with Compound 4, instead of thiosulfate, in equimolar quantity; three other samples with a + 30% molar quantity of Compound 4 as described before.

5 The results of these nine tests are shown in Table 2.

TABLE 2

10	Sensitizer	$\mu\text{M}/\text{Ag}$ mole	Ripening time at 55°C (minutes)	Fog	Speed	Y_M	Y_S (1)
	$\text{Na}_2\text{S}_2\text{O}_3$	53	100	0.23	1.22	2.23	1.27
15	"	"	150	0.36	1.12	2.55	1.67
	"	"	200	0.44	1.06	2.48	1.99
20	Compound 4	"	100	0.11	1.38	2.41	1.37
	"	"	150	0.16	1.26	2.82	2.05
25	"	"	200	0.19	1.22	2.79	2.09
	Compound 4	68	100	0.16	1.25	2.87	2.39
30	"	"	150	0.25	1.17	2.94	2.44
	"	"	200	0.35	1.13	2.82	2.69

35 (1) Y_S = shoulder contrast measured between the points D=2.10 and 3.10.

Example 11

A gelatin silver halide emulsion was prepared as described in Procedure C. Samples of the redispersed emulsion have been prepared: the first sample was added with thiosulfate solution, the second with Compound 1 solution; the third with Compound 2 solution, the fourth with Compound 4 solution, the fifth with Compound 5 solution and the last one with Compound 6 solution. Any product was added in equimolar quantity with respect to the thiosulfate. The samples of these emulsions have been digested for three times as described before and coated as usual. The results are shown in Table 3.

TABLE 3

	Sensitizer	$\mu\text{M}/\text{Ag}$ mole	Ripening time at 47°C (minutes)	Fog	Speed	γ_M	$D_{\max}$
5	$\text{Na}_2\text{S}_2\text{O}_3$	44	100	0.32	0.90	3.57	2.93
10	"	"	150	0.47	0.78	2.46	3.01
	"	"	200	(1.06)	—	—	3.05
15	Compound 1	44	100	0.13	1.10	4.31	2.93
	"	"	150	0.29	1.12	3.61	2.92
	"	"	200	0.81	0.98	1.88	2.95
20	Compound 2	44	100	0.11	1.12	3.98	2.87
	"	"	150	0.21	1.10	4.07	2.87
25	"	"	200	0.71	1.04	2.41	2.84
30	Compound 4	44	100	0.18	1.06	4.25	2.96
	"	"	150	0.58	0.86	2.78	3.03
	"	"	200	(0.94)	—	—	2.97
35	Compound 5	44	100	0.15	1.04	3.88	2.82
	"	"	150	0.17	1.02	4.27	3.00
40	"	"	200	0.24	1.03	3.82	2.98
45	Compound 6	44	100	0.10	1.28	1.86	2.61
	"	"	150	0.12	1.10	3.40	2.91
	"	"	200	0.13	1.07	3.67	2.89

Example 12

A gelatin silver halide emulsion was prepared as described in Procedure B. Samples of the digested emulsion have been added with equimolar solution of the $\text{Na}_2\text{S}_2\text{O}_3$, Compound 1 and Compound 2 chemical sensitizers. The samples were then digested for three times as described before and coated as usual. The sensitometric results are shown in Table 4.

TABLE 4

	Sensitizer	$\mu\text{M}/\text{Ag}$ mole	Ripening time at 56°C (minutes)	Fog	Speed	Y_M	Y_S	$D_{\max}$
5	$\text{Na}_2\text{S}_2\text{O}_3$	49	100	0.14	1.24	2.32	1.25	3.39
10	"	"	150	0.17	1.20	2.32	1.16	3.25
	"	"	200	0.19	1.15	2.35	1.23	3.33
15	Compound 1	49	100	0.06	1.37	2.14	—	3.06
	"	"	150	0.08	1.24	2.74	2.12	3.52
	"	"	200	0.10	1.21	2.60	1.60	3.39
20	Compound 2	49	100	0.06	1.35	2.30	1.49	3.37
	"	"	150	0.08	1.25	2.47	1.25	3.36
25	"	"	200	0.10	1.21	2.67	1.58	3.40

Example 13

30 A gelatin silver halide emulsion was prepared as described in Procedure B. Samples of the digested emulsion have been added with equimolar solutions of the $\text{Na}_2\text{S}_2\text{O}_3$, Compound 1, Compound 2 and Compound 4 chemical sensitizers; each sample has then been digested for three times as described before and coated as usual. The sensitometric results are shown below in Table 5.

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TABLE 5

5	Sensitizer	$\mu\text{M}/\text{Ag}$ mole	Ripening time at 56°C (minutes)	Fog	Speed	Y_M	Y_S	$D_{\max}$
	$\text{Na}_2\text{S}_2\text{O}_3$	49	100	0.17	1.30	2.91	2.15	3.89
10	"	"	150	0.20	1.24	2.64	1.89	3.69
	"	"	200	0.22	1.29	2.76	2.23	3.71
15	Compound 1	49	100	0.07	1.48	3.21	2.77	3.96
	"	"	150	0.12	1.35	2.87	2.95	4.00
20	"	"	200	0.19	1.36	3.01	2.21	4.01
	Compound 2	49	100	0.07	1.52	2.69	1.77	3.54
	"	"	150	0.08	1.48	2.85	2.27	3.75
25	"	"	200	0.09	1.44	2.89	2.54	3.87
	Compound 4	49	100	0.12	1.38	3.06	2.68	4.02
30	"	"	150	0.14	1.34	3.08	2.81	3.91
	"	"	200	0.15	1.34	3.19	2.99	4.09

Example 14

A gelatin silver halide emulsion was prepared as described in Procedure D. Samples of the digested emulsion were added with equimolar solution of the $\text{Na}_2\text{S}_2\text{O}_3$ and Compound 4 chemical sensitizers, then digested for three times as described before and coated as usual. The sensitometric results are shown below in Table 6.

TABLE 6

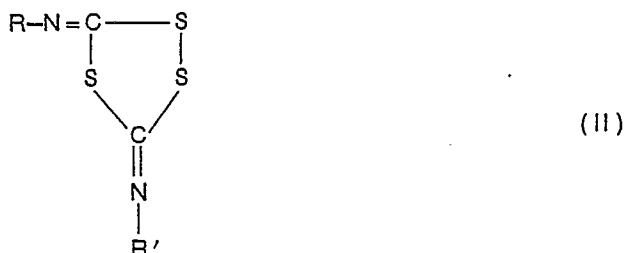
45	Sensitizer	$\mu\text{M}/\text{Ag}$ mole	Ripening time (minutes)	Fog	Speed	Y_M
	$\text{Na}_2\text{S}_2\text{O}_3$	30	100	0.39	1.91	1.57
50	"	"	150	0.68	1.75	1.30
	"	"	200	0.86	—	—
55	Compound 4	30	100	0.05	2.66	—
	"	"	150	0.05	2.44	—
60	"	"	200	0.04	2.27	2.39

Claims

1. A silver halide photographic emulsion associated with color couplers for the use in photography to obtain dye images, and containing a sensitizing amount of a sulfur sensitizer characterized by the fact that the sulfur sensitizer is a 1,2,4-dithiazolidino-3-thione sulfur sensitizer corresponding to the following formula:



or a dimethylenetrisulfide sulfur sensitizer corresponding to the following formula



or mixture thereof,

wherein R is a hydrogen atom, aliphatic group or an aromatic or non-aromatic cyclic nucleus and R' is a hydrogen atom, an aliphatic group or an aromatic or non-aromatic cyclic nucleus, at least one of them being different from hydrogen.

2. Photographic emulsion according to claim 1, wherein R and R' are both alkyl groups.

3. A photographic emulsion according to claim 2 wherein R and R' are alkyl groups with no more than 4 carbon atoms.

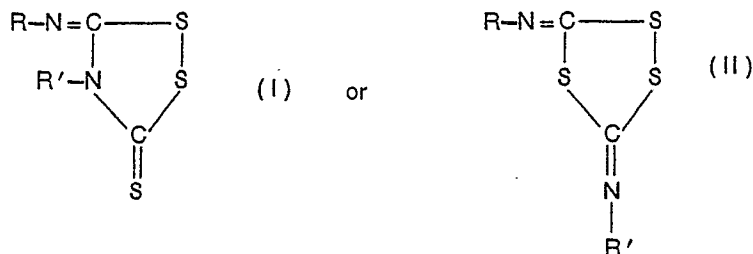
4. A photographic emulsion according to claim 3 wherein R and R' are methyl.

5. A photographic emulsion according to claim 1 wherein R and R' independently comprise alkyl groups of no more than 4 carbon atoms and phenyl groups.

6. A photographic emulsion according to claim 1, containing also a sensitizing amount of noble metal salt sensitizer.

7. A photographic element including a supporting base and a silver halide photographic emulsion associated with colour couplers and containing a sensitizing amount of a sulphur sensitizer, characterized in that the sulphur sensitizer is as defined in Claim 1.

8. Method of manufacturing a silver halide photographic emulsion for use in color photography which includes the addition of at least one sulfur sensitizing compound, characterized in that said compound has the formula:



or mixture thereof,

wherein R is a hydrogen atom, aliphatic group or an aromatic or non-aromatic cyclic nucleus and R' is a hydrogen atom, an aliphatic group, or an aromatic or non-aromatic cyclic nucleus, at least one of them being different from hydrogen to the silver halide emulsion prior to or during the chemical digestion and the subsequent addition of a color coupler prior to the coating of the obtained photographic composition.

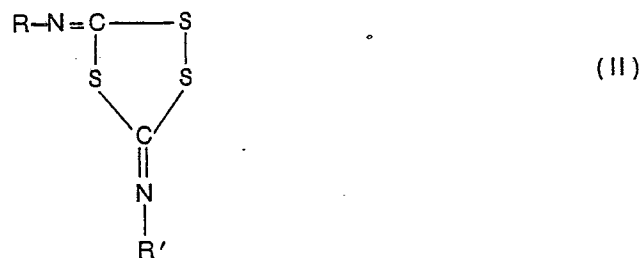
9. The method of claim 8 wherein R and R' are independently selected from alkyl groups of no more than 4 carbon atoms.

Patentansprüche

1. Photographische Silberhalogenidemulsion, der Farbkupplern zum Herstellen von Farbstoffbildern in der Photographie zugeordnet sind und die eine sensibilisierend wirkende Menge eines Schwefelsensibilisators enthält, dadurch gekennzeichnet, daß der Schwefelsensibilisator eine 1,2,4-Dithiazolidino-3-thion-Schwefelsensibilisator der Formel



oder ein Dimethylentrisulfid-Schwefelsensibilisator der Formel



oder ein Gemisch derselben ist, wobei R ein Wasserstoffatom, eine aliphatische Gruppe oder ein aromatischer oder nichtaromatischer zyklischer Kern und R' ein Wasserstoffatom, eine aliphatische Gruppe oder ein aromatischer oder nichtaromatischer zyklischer Kern ist und mindestens eines von ihnen etwas anderes ist als Wasserstoff.

2. Photographische Emulsion nach Anspruch 1, dadurch gekennzeichnet, daß sowohl R als auch R' Alkylgruppen sind.

3. Photographische Emulsion nach Anspruch 2, dadurch gekennzeichnet, daß sowohl R als auch R' Alkylgruppen mit nicht mehr als 4 Kohlenstoffatomen sind.

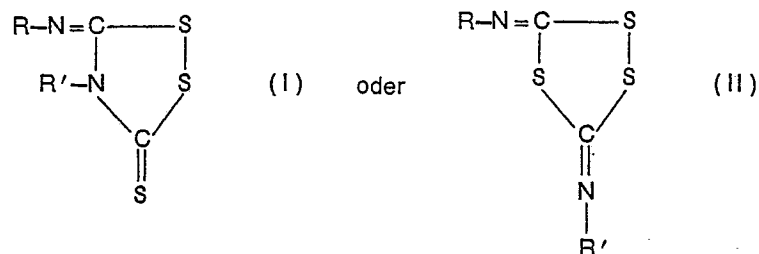
4. Photographische Emulsion nach Anspruch 3, dadurch gekennzeichnet, daß R und R' Methyl sind.

5. Photographische Emulsion nach Anspruch 1, dadurch gekennzeichnet, daß R und R' unabhängig voneinander Alkylgruppen mit nicht mehr als 4 Kohlenstoffatomen und Phenylgruppen enthalten.

6. Photographische Emulsion nach Anspruch 1, dadurch gekennzeichnet, daß sie ferner eine sensibilisierend wirkende Menge eines Edelmetallsalz-Sensibilisators enthält.

7. Photographisches Element mit einem Träger und einer photographischen Silberhalogenidemulsion, der Farbkuppler zugeordnet sind und die eine sensibilisierend wirkende Menge eines Schwefelsensibilisators enthält, dadurch gekennzeichnet, daß der Schwefelsensibilisator dem in Anspruch 1 Angegebenen entspricht.

8. Verfahren zum Erzeugen einer photographischen Silberhalogenidemulsion für die Verwendung in der Farbphotographie, in dem mindestens eine Schwefelsensibilisatorverbindung zugesetzt wird, dadurch gekennzeichnet, daß die genannte Verbindung die Formel



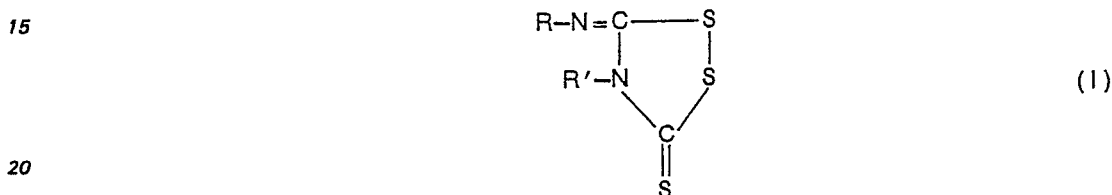
hat oder aus einem Gemisch derselben bestehender Schwefelsensibilisator zugesetzt wird, wobei R ein Wasserstoffatom, eine aliphatische Gruppe oder ein aromatischer oder nichtaromatischer zyklischer Kern und R' ein Wasserstoffatom, eine aliphatische Gruppe oder ein aromatischer oder nichtaromatischer zyklischer Kern ist und mindestens eines von ihnen etwas anderes ist als Wasserstoff, wobei diese

Verbindung der Silberhalogenidemulsion vor oder während des chemischen Aufschlusses zugesetzt wird und danach ein Farbkuppler zugesetzt wird, bevor die so erhaltene photographische Zusammensetzung zur Bildung eines Überzuges aufgetragen wird.

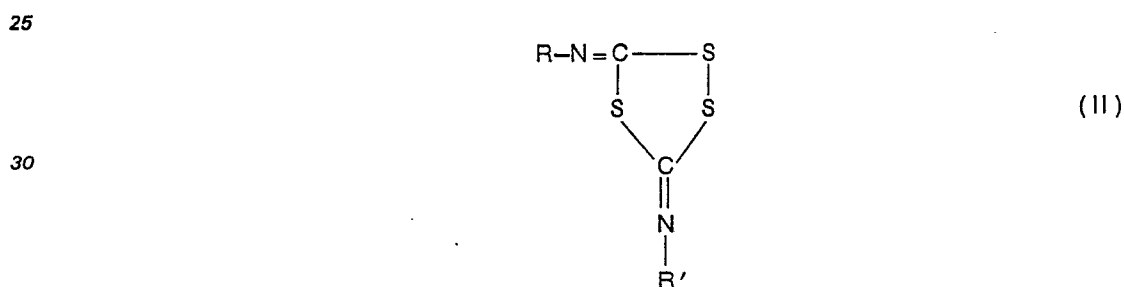
9. Verfahren nach Anspruch 8, dadurch gekennzeichnet, daß R und R' unabhängig voneinander aus den Alkylgruppen mit nicht mehr als 4 Kohlenstoffatomen ausgewählt sind.

Revendications

1. Une émulsion photographique d'halogénure d'argent associée à des coupleurs chromogènes pour l'emploi en photographie afin d'obtenir des images de colorant et contenant une quantité sensibilisante d'un sensibilisateur sulfuré, caractérisée par le fait que le sensibilisateur sulfuré est un sensibilisateur sulfuré de type 1,2,4-dithiazolidino-3-thione correspondant à la formule suivante



ou un sensibilisateur sulfuré de type diméthylènetrisulfure correspondant à la formule suivante:



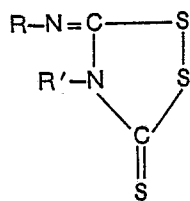
ou un de leurs mélanges,

où R est un atome d'hydrogène, un groupe aliphatique ou un noyau cyclique aromatique ou non aromatique et R' est un atome d'hydrogène, un groupe aliphatique ou un noyau cyclique aromatique ou non aromatique, au moins un d'entre eux différent de l'hydrogène.

- 40 2. Emulsion photographique selon la revendication 1 dans laquelle R et R' sont tous deux des groupes alkyles.
3. Une émulsion photographique selon la revendication 2 dans laquelle R et R' sont des groupes alkyles n'ayant pas plus de 4 atomes de carbone.
- 45 4. Une émulsion photographique selon la revendication 3 dans laquelle R et R' sont un méthyle.
5. Une émulsion photographique selon la revendication 1 dans laquelle R et R' sont constitués indépendamment de groupes alkyles n'ayant pas plus de 4 atomes de carbone et de groupes phényles.
6. Une émulsion photographique selon la revendication 1 contenant également une quantité sensibilisante d'un sensibilisateur constitué d'un sel de métal noble.
- 50 7. Un élément photographique comprenant une base support et une émulsion photographique d'halogénure d'argent associée à des coupleurs chromogènes et contenant une quantité sensibilisante d'un sensibilisateur sulfuré, caractérisé en ce que le sensibilisateur sulfuré est comme défini dans la revendication 1.
8. Procédé de préparation d'une émulsion photographique d'halogénure d'argent pour l'emploi en photographie en couleurs qui comprend l'addition d'au moins un composé sensibilisant sulfuré caractérisé en ce que ledit composé a pour formule:
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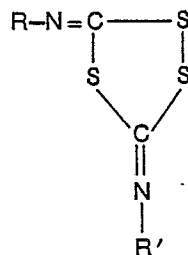
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(I)

ou



(II)

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ou un de leurs mélanges,

où R est un atome d'hydrogène, un groupe aliphatique ou un noyau cyclique aromatique ou non aromatique et R' est un atome d'hydrogène, un groupe aliphatique ou un noyau cyclique aromatique ou non aromatique, au moins un d'entre eux différent de l'hydrogène, à l'émulsion d'halogénure d'argent avant ou pendant la digestion chimique et l'addition ultérieure d'un coupleur chromogène avant la formation du revêtement de la composition photographique obtenue.

9. Le procédé de la revendication 8 dans lequel R et R' sont choisis indépendamment parmi les groupes alkyles n'ayant pas plus de 4 atomes de carbone.

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