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3,364,028

**PHOTOGRAPHIC MATERIAL CONTAINING
YELLOW FOG-PREVENTING AGENTS**

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8 Claims. (Cl. 96-84)

ABSTRACT OF THE DISCLOSURE

Yellow fog formation in silver halide emulsion supports, particularly where the support surface is a baryta layer, can be avoided by adding to the emulsion or baryta layer or both a heterocyclic compound having a 5 to 6 membered nitrogen-containing heterocyclic ring substituted with a member selected from the group consisting of esterified carboxyl and esterified thiocarboxyl, said substituent being directly bonded to a ring nitrogen, or through only a sulfur or oxygen atom to a ring carbon in alpha position to a ring nitrogen, said heterocyclic compound being capable of splitting off said substituent and forming difficultly soluble silver compounds.

This invention relates to an improved photographic material comprising a silver halide emulsion layer and containing an organic compound which is capable of preventing the formation of yellow fog.

In the processing of photographic materials, thiosulfate is frequently transferred from the fixing bath into the developer. On other occasions, such as when using high-speed, stabilizing or fixing developers, a silver halide solvent, generally thiasulfate, is added to the developer. When such developers containing silver halide solvents are used in the development of photographic materials, a yellow to brown fogging is produced, of varying intensity depending on the type and the age of the photographic paper. In the presence of many stabilizers, e.g. 1-phenyl-5-mercapto-tetrazole, this fogging may also be blue to bluish violet in color. With photographic papers, this fogging is due to finely divided silver deposited in the baryta-coating.

This yellow fogging produced with baryta-coated photographic papers results from the passing, during the casting process, of silver salts from the silver halide emulsion into the baryta coating where they are adsorbed by the baryta. During the storage of the papers, these silver salts are reduced to silver, particularly in the first months of storage. If the developer used in the processing of such papers contains silver halide solvents, such as thiosulfates, the dissolved silver salts are reduced on the silver nuclei of the baryta and a yellow fogging and spot formation is produced. Furthermore, the properties of the starting materials play a large part in the formation of spots or stains.

After storage, the yellow fogging appears particularly strongly at those areas of the papers which were exposed to the humidity of the air, i.e. at the edges of the papers and on the uppermost sheet of a pack.

This yellow fogging occurs particularly when using unwashed silver chloride or chlorobromide emulsions because the chlorides present in excess are able to form soluble silver complex salts.

This yellow fogging also occurs if, in the production of the emulsion or the baryta, types of gelatin are used which contain compounds capable of dissolving silver halide and if in addition nucleus-forming degradation products of the gelatin are present. Such types of gelatin also cause

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a yellow fogging with photographic films. In addition, emulsions which have only just ripened and have a steep gradation are particularly liable to produce yellow fogging when steeply operating developers with a relatively high content of potassium bromide are used for developing the silver image.

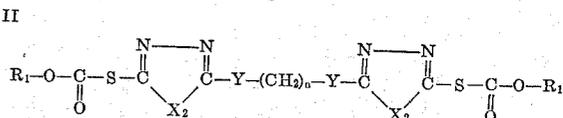
It has now been found that yellow fogging can be avoided by using photographic materials which contain in a hydrophilic, water permeable colloid layer, e.g. the silver halide emulsion layer and/or the baryta coating, substances of the following general formula:



wherein R represents a nitrogen-containing heterocyclic ring system, X represents sulfur or oxygen bonded to a carbon atom of the heterocyclic ring, R₁ represents alkyl, cycloalkyl, aryl, aralkyl and Z represents oxygen or sulfur.

In the above formula suitable heterocyclic ring systems R are the ring systems of diazoles, oxazoles, triazoles, imidazoles, thiazoles, thiadiazoles, thiadiazolidines, oxadiazoles, tetrazoles, diazines, triazines, imidazolines, benzthiazoles, benzoxazoles, benzimidazoles, naphtriazoles, benztriazoles, quinoline, pyrimidine, partially hydrogenated pyrimidine, quinazoline, quinoxaline, purine, azaindolizines or other heterocyclic ring systems which form part of heterocyclic compounds that are capable of forming difficultly soluble silver salts and which are used in the photographic art as stabilizers or antifoggants for silver halide emulsions. The heterocyclic ring systems are derived from said heterocyclic compounds by subtracting therefrom a mercapto or hydroxy group which is bonded to the heterocyclic system or by subtracting therefrom a hydrogen atom which is bonded to nitrogen atom forming part of the heterocyclic system.

A suitable class of compounds may more specifically be represented by the following formula:

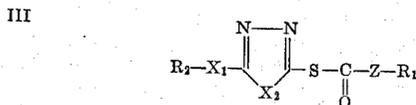


wherein Y represents S, NH, or a chemical bond, X₂ represents sulfur or oxygen, n represents an integer from 0 to 10, and R₁ has the same meaning as in Formula I.

Representative of this class of compounds are the following:

1. Y=S; n=2; R₁=C₂H₅; X₂=S; M.P., 118° C.
2. Y=S; n=4; R₁=C₂H₅; X₂=S; M.P., 146° C.
3. Y=NH; n=6; R₁=C₂H₅; X₂=S; M.P., 144° C.
4. Y=chem. bond; n=2; R₁=C₂H₅; X₂=O; M.P., 146° C.
5. Y=chem. bond; n=8; R₁=C₂H₅; X₂=O; M.P., 80° C.

A further class of suitable compounds may more specifically be represented by the following formula:



wherein R₂ represents alkyl having 1 to 18 carbon atoms, cycloalkyl or carboxyalkyl, preferably up to 5 carbon atoms, X₁ represents S, NH or a chemical bond, X₂ represents S, NH, N-alkyl, N-alkenyl or



and Z and R₁ have the same meaning as in Formula I.

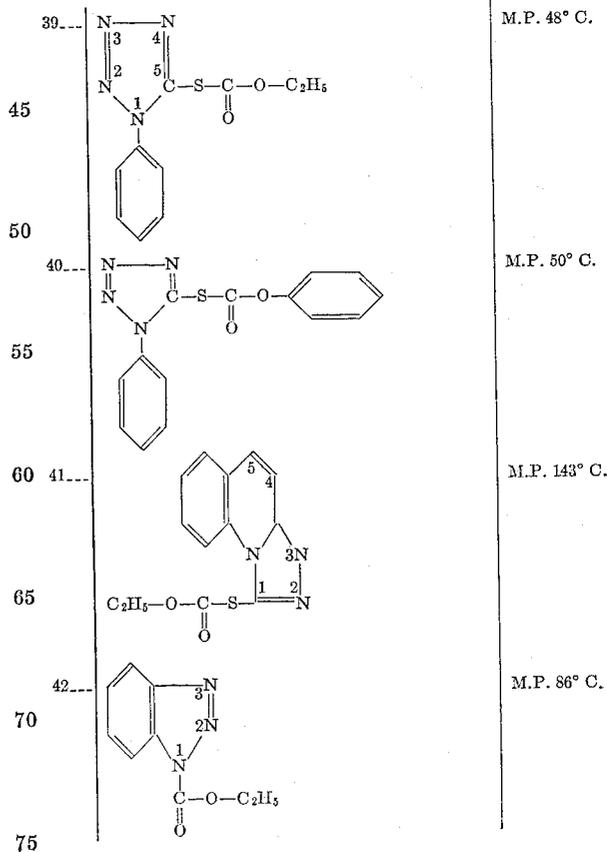
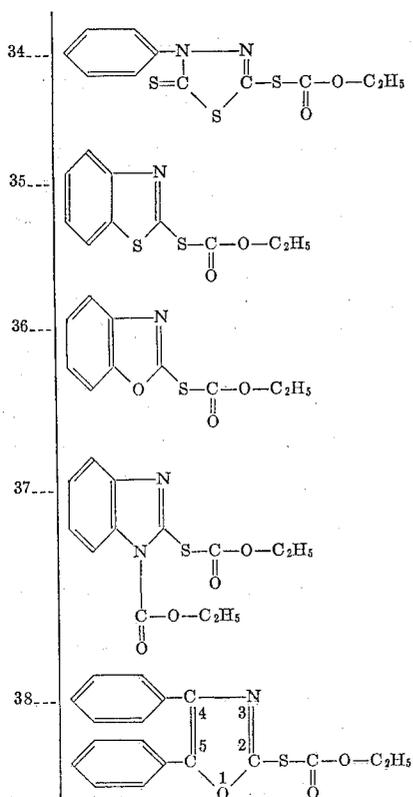
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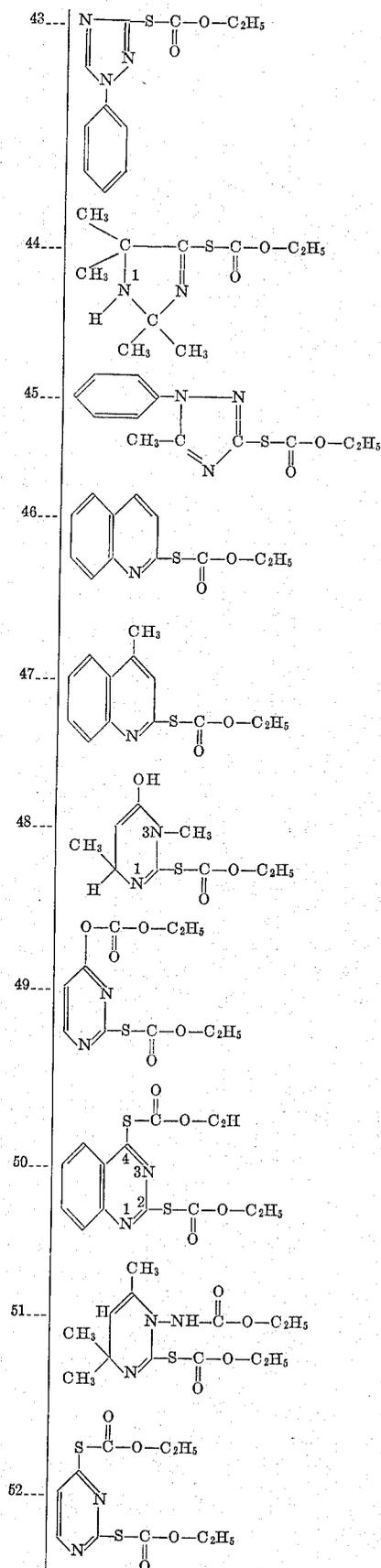
Representatives of this last mentioned class of compounds are:

	X ₂	X ₁	Z	R ₂	R ₁	M.P., ° C.
6.....	S	S	O	methyl	ethyl	38
7.....	S	S	O	methyl	methyl	41
8.....	S	S	O	methyl	phenyl	57
9.....	S	S	O	ethyl	ethyl	39
10.....	S	S	O	ethyl	methyl	41
11.....	S	S	O	ethyl	phenyl	52
12.....	S	S	O	n-propyl	ethyl	Fluid
13.....	S	S	O	isopropyl	ethyl	Fluid
14.....	S	S	O	sec. butyl	ethyl	Fluid
15.....	S	S	O	n-butyl	ethyl	39
16.....	S	S	O	n-butyl	methyl	Fluid
17.....	S	S	O	n-butyl	phenyl	Fluid
18.....	S	S	S	n-butyl	ethyl	Fluid
19.....	S	S	S	n-butyl	phenyl	58
20.....	S	S	O	n-pentyl	ethyl	Fluid
21.....	S	S	O	n-pentyl	methyl	Fluid
22.....	S	S	O	n-hexyl	ethyl	39
23.....	S	S	O	n-octyl	ethyl	33
24.....	S	S	O	n-octyl	methyl	35
25.....	S	S	O	n-octyl	phenyl	(i)
26.....	S	S	O	$\begin{array}{c} \text{---C---O---C}_2\text{H}_5 \\ \\ \text{O} \end{array}$	ethyl	81
27.....	S	NH	O	n-dodecyl	ethyl	67
28.....	S	NH	O	cyclohexyl	ethyl	129
29.....	N CH ₃	chem. bond	O	methyl	ethyl	75
30.....	N CH ₃	chem. bond	O	methyl	phenyl	142
31.....	N CH ₂ -CH=CH ₂	chem. bond	O	methyl	ethyl	(i)
32.....	N CH ₂ -CH=CH ₂	chem. bond	O	methyl	phenyl	78
33.....	C / \ \\ CH ₃ CH ₃	chem. bond	O	methyl	ethyl	89

¹ Highly viscous fluid.

Further specific examples of suitable compounds are those of the following formulae:





M.P. 78° C.

M.P. 154° C.

M.P. 41° C.

Highly viscous fluid.

M.P. 59° C.

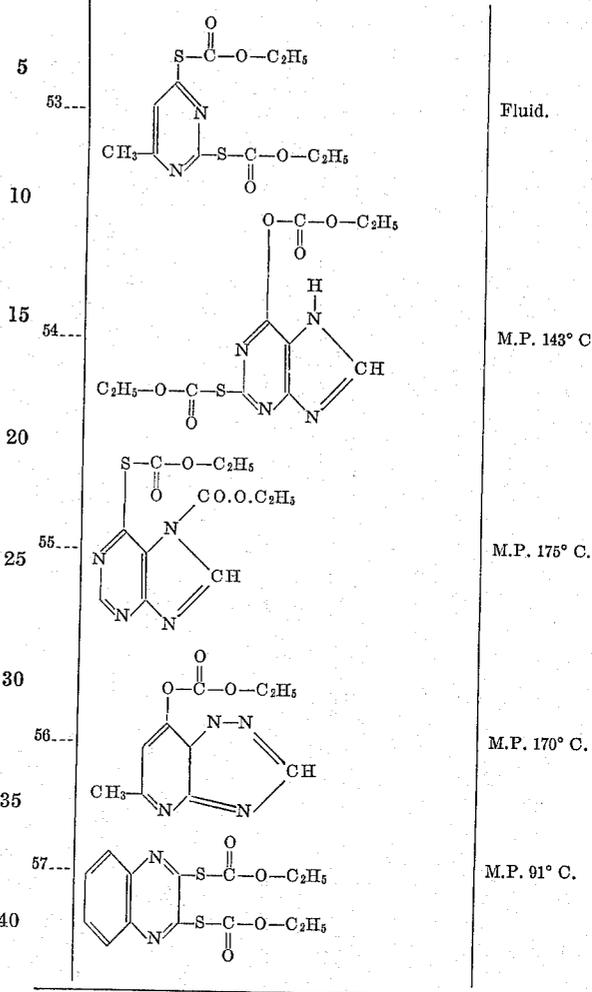
Fluid.

Highly viscous fluid.

M.P. 79° C.

Highly viscous liquid.

Fluid.



Fluid.

M.P. 143° C.

M.P. 175° C.

M.P. 170° C.

M.P. 91° C.

- 45 The compounds may be produced by reaction of about equivalent amounts of the heterocyclic compounds containing either a hydrogen atom bonded to a heterocyclic nitrogen atom or a mercapto or hydroxy group bonded to a carbon atom of the heterocyclic nucleus with chloroformic or chlorothioformic acid esters in the presence of sodium hydroxide in acetone or dioxane at temperatures of 0-40° C. The crude products which are not soluble in ether are purified by washing with water and recrystallizing. The other crude products are dissolved in ether and after evaporation of the ether recrystallized from suitable solvents. These processes are illustrated by the following examples.

Production of compound 23.—26.2 g. ($\frac{1}{10}$ mol) of 2-octylthio-5-mercapto-1,3,4-thiadiazole are suspended in

- 40 cc. of 10% sodium hydroxide solution with addition of 300 cc. of acetone. 9.6 cc. ($\frac{1}{10}$ mol) of ethyl chloroformate are added to the suspension with stirring at 0 to 5° C. After distilling off the acetone, the residue is extracted with ether. The ethereal solution is washed neutral, dried, and the ether distilled off. The crude product is recrystallized from methanol. Yield 17 g. Melting point 33° C.

Production of compound 56.—15 g. of 6-methyl-4-hydroxy-1,3,3a,7-tetraazaindene are suspended in 150 cc.

- 40 of acetone with addition of 20 cc. of 20% sodium hydroxide solution. 9.6 cc. of ethyl chloroformate are added to the suspension with stirring at 0 to 5° C. After distilling off the acetone, the residue is purified by washing with ether and recrystallized from acetone. Yield 4.2 g. Melting point 170° C.

Compound 42 is set out in Beilstein, vol. 26, page 40.

Methanol is used for recrystallizing compounds 1, 9, 10, 15, 16, 22, 24, 26, 27, 28, 29, 38, 39, 44, toluene for recrystallizing compound 2 and petrolether for recrystallizing compound 8. Compounds 6, 7, 35, 36, 43 are purified by dissolving the raw products in ether, washing the ethereal solution with water, evaporating the ether, dissolving the residue in methanol and precipitating with water. The raw product of compound 3 is purified by dissolving it in methylenechloride, evaporating the solvent, reprecipitating the residue from dimethylformamid and water and dissolving the precipitate in ether and evaporating the ether. The raw products of compounds 4 and 5 are first dissolved in methylenechloride, the methylenechloride is evaporated, the residue is redissolved in petrolether and the solvent is evaporated. The raw products of compounds 11, 12, 13, 14, 17, 18, 19, 20, 21, 25, 31, 33, 34, 37, 40, 45, 46, 47, 49, 50, 51, 52, 53, 57 are purified by dissolving them in ether, washing the ethereal solution with water, evaporating the ether, redissolving the residue in ether, methanol and acetone and each time evaporating the solvent. The raw products of compounds 30, 54 are purified by dissolving them in methylenechloride or dioxane respectively and evaporating the solvent.

The substances of the present invention are probably not adsorbed by the silver halide grains of the emulsion, but are disposed in the gelatin phase between the silver halide grains. In the alkaline developer, the carboxy group is split off and the compound reacts with the soluble silver salts, thus preventing the formation of yellow fogging.

As silver halide emulsion, it is possible to use emulsions containing silver chloride or silver bromide or mixtures thereof. Furthermore, the emulsion may contain up to about 10% of silver iodide, as calculated on total silver halide.

As binding agents for the baryta layer can be used animal glues preferably gelatin which may be partially replaced by film-forming hydrophilic products such as polyvinyl alcohol, polyvinyl-pyrrolidone, alginic acid or derivatives thereof such as alkali metal salts, esters in particular with lower aliphatic glycols, or amides, and in addition, carboxyethylcellulose, starch or the like. As baryta pigment can be used mineral products such as processed heavy spar or artificial products such as permanent white or blanc fixe.

The compounds according to the invention can be added to any desired layer of the photographic material, but advantageously to the baryta and/or light-sensitive silver halide emulsion layer. It will depend on the photographic material and the compound in which layer the optimum efficacy is achieved. However, this can be established by a few simple experiments without any difficulties.

The same applies as regards the concentration to be used. The quantities to be added depend on the layer in which the compounds are incorporated and this can also be established by simple tests. When used in the emulsion layer, the compounds are added in amounts of about 2-300 mg., advantageously 5-60 mg. per mol of silver halide. For the baryta layer, concentration of 0.01-1.0 g./l. and advantageously 0.05-0.15 g./l. of casting solution are suitable. These amounts correspond to 0.02-2 mg., preferably 0.04-0.3 mg. per gram of barium sulfate.

The compounds according to the invention can be added at any time, but advantageously to the prepared casting solution.

The photographic emulsions can be either sensitized or non-sensitized optically. In addition, other chemical ripening compounds can also be added to them, for example sulfur compounds or noble metal salts. The emulsions can further contain alkylene oxide polymerization products as chemical sensitizers. Moreover, the new stabilizers can be used together with other stabilizers which are already known. They can furthermore be used in

emulsions which contain color couplers or silver halide developer substances.

In the processing of the photographic materials according to the invention, it is possible to employ the conventional developer combinations. The process does not depend on any particular developer substances. It is for example possible to use as developer substances hydroquinone, pyrocatechol, p-methylaminophenol, 1-phenyl-3-pyrazolidones or phenylene diamines.

Example 1

An unrinsed silver chlorobromide emulsion containing 0.12 mol of silver halide per litre, has added thereto, prior to casting, 2 mg. of compound 15 dissolved in alcohol. After adding the conventional hardening and wetting agents, the emulsion is then applied in known manner to a baryta-coated paper and dried. The paper, both when fresh and after being kept for 2 days in a hot cupboard at 60° C., was developed for 1, 2, 3, 5 and 7 minutes at 30° C. in a p-methylaminophenol-hydroquinone developer, to which 10 g./l. of crystallized sodium thiosulfate had been added in order to test for yellow fogging. Whereas the specimen showed no yellow fogging, even after storage in the heated cupboard, a control specimen when fresh showed a slight yellow fogging, and after being kept in the cupboard a strong brownish-yellow fogging was visible, even after a development time of 1 minute. If the emulsion layer is removed from the baryta coating, it is seen that the baryta coating of the control specimen is brown in colour and that of the test specimen is colorless.

Instead of compound 15 referred to above, the following can also be added to the emulsion with the same result:

20 mg./l. of compound 16, 20 mg./l. of compound 23, 5 mg./l. of compound 37, 15 mg./l. of compound 42 or 15 mg./l. of compound 35.

Example 2

One liter of silver chloride emulsion, containing 0.08 mol of silver halide, has 5 mg. of compound 39, dissolved in alcohol, added thereto prior to casting. After adding the usual hardening and wetting agents, the emulsion is then applied in known manner to a baryta-coated paper and dried. The test for yellow fogging is carried out as described in Example 1. Whereas the control specimen shows a bluish-yellow fogging after being kept in the heated cupboard, no fogging is visible with the specimen according to the invention. Instead of the aforementioned compound 39 it is also possible for 5 mg./l. of compound 36 or 10 mg./l. of compound 52 to be added to the emulsion with the same result.

Example 3

A phototechnical emulsion, which contains about 0.4 mol./l. of silver halide (silver iodobromide emulsion), has 5 mg. of compound 56, dissolved in alcohol, added thereto prior to casting. After adding the usual hardening and wetting agents, the emulsion is applied in known manner to a film or paper support and dried.

The test for yellow fogging is carried out as described in Example 1. The specimen does not show any yellow fogging, whereas a yellow fogging is visible on the control specimen after being stored in the heated cupboard.

Instead of the aforementioned compound 56, it is possible with the same result to add to the emulsion 1 mg./l. of compound 28.

Example 4

A baryta-coating solution has added thereto 0.15 g./l. of the compound 2, dissolved in alcohol, and a paper is baryta-coated therewith three times in known manner. An unrinsed silver chlorobromide emulsion is thereafter applied to this paper in known manner. The baryta-coating solution may be obtained in known manner from 15 kg. of barium sulfate (containing 20% of water), 1.5 kg. of gelatin in the form of a 5% aqueous solution, 100 cm.³ of a 20% aqueous sodium hexametaphosphate solution, 300

cm.³ of a 10% aqueous chrome alum solution and 200 cm.³ of milk. Instead of compound 2 the baryta coating solution may have added thereto per liter 30 mg. of compound 10, 12 or 15, 20 mg. of compound 28 or 50 mg. of compound 35.

The test for yellow fogging is carried out as described in Example 1. Whereas the experimental samples shows no yellow fogging after the heated chamber storage, a dark brown patchy yellow fogging is visible with the control specimen.

What I claim is:

1. A photographic material comprising a support carrying a light sensitive silver halide emulsion layer, said emulsion being in contact with a heterocyclic compound having a 5 to 6 membered nitrogen containing heterocyclic ring substituted with a member selected from the group consisting of esterified carboxyl and esterified thiocarboxyl, said substituent being bonded directly to a ring nitrogen, or through only a sulfur or oxygen atom to a ring carbon in α -position to a ring nitrogen, said heterocyclic being capable of splitting off said substituent and forming difficultly soluble silver compounds and being present in amount sufficient to substantially inhibit the formation of yellow fog.

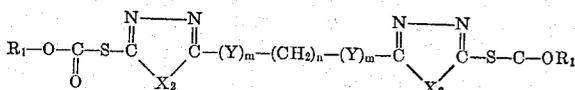
2. A photographic material according to claim 1, wherein said support is coated with a baryta layer which is arranged between said support and said silver halide emulsion layer.

3. A photographic material according to claim 1, wherein said heterocyclic ring contains 1 to 4 nitrogen atoms.

4. A photographic material according to claim 1, wherein said heterocyclic ring is a five membered ring containing one to two nitrogen atoms and a sulfur atom.

5. A photographic material according to claim 1, wherein said heterocyclic ring contains a nitrogen and an oxygen atom.

6. A photographic material comprising a support, a baryta layer and a silver halide emulsion layer, the baryta layer being arranged between the support and the silver halide emulsion layer, at least one of said layers containing a heterocyclic compound of the formula



wherein:

R_1 is a member of the group consisting of alkyl having 1 to 18 carbon atoms, cycloalkyl, aryl and aralkyl,

Y a member of the group consisting of sulfur, oxygen and nitrogen;

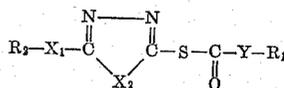
X_2 a member of the group consisting of sulfur and oxygen;

n an integer of 0 to 10; and

m an integer of 0 to 1.

said heterocyclic compound being present in amount sufficient to substantially inhibit the formation of yellow fog.

7. A photographic material comprising a support, a baryta layer and a silver halide emulsion layer, the baryta layer being arranged between the support and the silver halide emulsion layer, at least one of said layers containing a heterocyclic compound of the formula



wherein:

R_1 is a member of the group consisting of alkyl having 1 to 18 carbon atoms, cycloalkyl, aryl and aralkyl;

R_2 is a member of the group consisting of alkyl having 1 to 18 carbon atoms, cycloalkyl, and carboxyalkyl;

X_1 is a member of the group consisting of sulfur and nitrogen;

X_2 is a member of the group consisting of S, NH, N-alkenyl and



the alkyl groups having 1 to 6 carbon atoms; and

Z is a member of the group consisting of sulfur and oxygen,

said heterocyclic compound being present in amount sufficient to substantially inhibit the formation of yellow fog.

8. A photographic material according to claim 1 in which the heterocyclic ring is a thiodiazole ring and the substituent is connected through a sulfur atom to a ring carbon.

References Cited

UNITED STATES PATENTS

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2,939,789	6/1960	Dersch et al.	96-109
3,212,892	10/1965	Konig et al.	96-129

NORMAN G. TORCHIN, *Primary Examiner*.

J. H. RAUBITSCHKE, *Assistant Examiner*.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

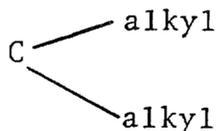
Patent No. 3,364,028

January 16, 1968

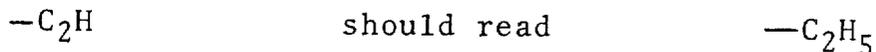
Anita von König

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

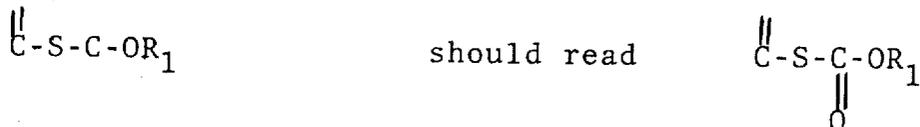
Column 1, line 36, "thiasulfate" should read -- thiosulfate --. Column 2, lines 67 to 69, the formula should appear as shown below:



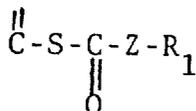
Column 5, formula 50, the right-hand portion reading



Column 6, formula 54, "M.P. 143° C." should read -- D.P. 143° C. --; line 72, "suspensoin" should read -- suspension --. Column 9, lines 43 to 45, the right-hand portion of the formula reading



Column 10, lines 14 to 16, the right-hand portion of the formula should appear as shown below:



Signed and sealed this 18th day of November 1969.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents