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3,148,987

PHOTOGRAPHIC MATERIAL

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3 Claims. (Cl. 96-109)

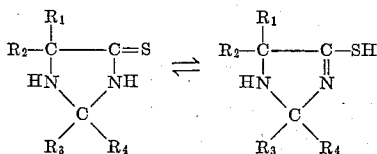
The present invention relates to fog inhibiting compounds and stabilizers for light-sensitive photographic emulsions and also to the use of these compounds in light-sensitive photographic material.

It is known that light-sensitive photographic emulsions, on storage in a place of a high temperature and a high relative humidity or wherein these materials come into contact with some substances such as hydrogen sulphide, hydrogen peroxide vapours or reducing agents, tend to lose their sensitivity and become spontaneously developable without any preliminary exposure. This phenomenon is called chemical fog as to differentiate it from the light fog due to an undesired exposure. The fog formation depends on the emulsion type and is directly proportional to the age, the temperature and the relative humidity on storage.

It is also known that the silver image formed after exposure undergoes a degradation, by which is meant a shift and a decrease of intensity of the image tone during the finishing to a visible image e.g. under the influence of ingredients used in the developing bath, the fixing bath, the colouring bath, and so on. This degradation especially appears on drying the developed images, whereby a decrease of density and of gradation and the appearance of an undesired colour or metallic gloss of the developed silver, the so called "plumming," is stated. This phenomenon is particularly pronounced when the photographic images are submitted to hot glazing.

Several compounds have been proposed to be used as stabilizers, fog-inhibiting agents or anti-bronzing agents. The greater part of these compounds, however, presents the draw-back of being only active within well definite limits and of usually exerting a strong desensitizing action onto the emulsion.

It has now been found that the imidazolidine-4-thiones and their tautomers corresponding to the following general formula



wherein:

Each of R_1 , R_2 , R_3 and R_4 (equal or different) represents a hydrogen atom, an alkyl radical, a substituted alkyl radical, an alkaryl radical, a substituted alkaryl radical, an aryl radical or a substituted aryl radical; or

R_1 and R_2 , and also R_3 and R_4 two by two represent the atoms necessary to close a saturated homocyclic nucleus or a substituted saturated homocyclic nucleus,

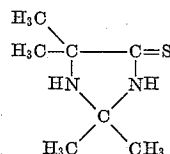
are effective anti-bronzing agents and exert a stabilizing and a fog-inhibiting action onto light-sensitive photographic emulsions without impairing their sensitivity.

Some compounds according to the present invention

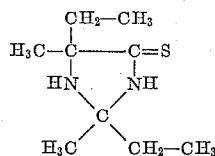
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which appeared from the experiments to give particularly good results are identified hereinafter:

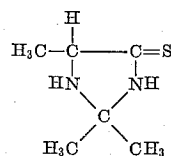
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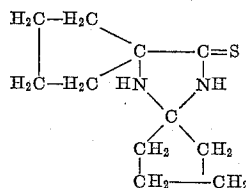
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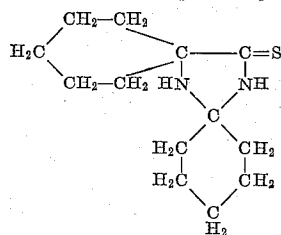
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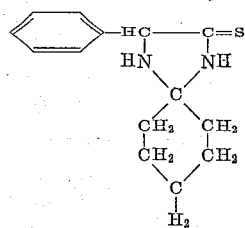
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(6)



These compounds may be prepared according to known methods as e.g. those described by J. D. Christian, J. Org. Chem., 22 (1957), 398; Bucherer and Brandt, J. prakt. Chem., 140 (1934), 129; U.S. patent specifications 2,785,175 and 2,806,036; C. A. 28, 4383 with reference to Science Repts., Tokyo Bunrika Daigaku, Sect. A. 2, 1-7 (1934), and C. A. 22, 2146.

The preparation for the greater part corresponds with the reaction of ketone cyanohydrines with ammonium sulfide.

The compounds according to the present invention preferably are added to the emulsion after the second ripening or just before coating.

Instead of adding these compounds to the silver halide emulsion itself, they can also be added to a water-perme-

able layer such as a gelatin covering layer or to an intermediate layer adjacent to the emulsion layer. The used emulsions may be sensitized according to a usual process. They may be chemically sensitized by little quantities of sulphurous compounds such as allyl isothiocyanate, allyl thiourea, sodium thiosulfate, etc. The emulsions may also be sensitized by means of reducing agents e.g. the tin compounds described in the Belgian patent specifications 493,464 and 568,687, the imino-aminomethane sulphinic acid compounds described in the Belgian patent specification 547,323, and small quantities of noble metal compounds e.g. of gold, platinum, palladium, iridium, ruthenium and rhodium. The emulsion may also be sensitized by means of polyalkylene oxide derivatives e.g. polyethylene oxide, the molecular weight of which varying between 1000 and 20,000 condensation products of alkylene oxides with aliphatic alcohols or glycols, with cyclic dehydrated products of hexitols, with alkyl substituted phenols, with aliphatic carboxylic acids, with aliphatic amines and diamines, and with aliphatic amides. The condensation products may have a molecular weight of at least 700 and preferably above 1000.

In order to obtain well defined effects, these sensitizers evidently may be applied in combination, such as described e.g. in the Belgian patent specification 537,278 and in the British patent specification 727,982.

Further these compounds may be applied in optically sensitized emulsions as well as in non-optically sensitized emulsions.

In order to obtain well defined effects, these compounds may also be used in combination with other known stabilizers, e.g. 7-hydroxy-5-alkyl-s-triazolo(2,3-a)pyrimidines e.g. in high-sensitive emulsions containing a development activator of the polyoxalkylene type.

The compounds according to this invention may be applied to all kinds of emulsions such as silver bromide emulsions containing a considerable amount of silver iodide, silver bromide emulsions, silver bromide containing silver chloride emulsions, and silver chloride emulsions, thus in all the usual negative and positive kinds of photographic films and papers. Especially in emulsions of photographic paper sorts which after development are submitted to high-glossing, the compounds according to this invention are very efficient as "antibronzing"-agents.

The quantity of stabilizers may vary according to the kind of the used silver halide or a mixture thereof, the degree of ripening, the presence or the absence of other emulsion additives such as colour couplers, optical bleaching agents, anti-oxidation agents, substances influencing the image-tone, etc. Generally the quantity of stabilizer varies between 0.001 and 0.35 g. per mol of silver halide. In some circumstances, however, e.g. in order to achieve determined effects, larger amounts may be used.

The following examples illustrate the invention, without limiting, however, the scope thereof.

Example 1

To different samples of the same high-sensitive silver bromo-iodide emulsion (about 3.5% of iodide), amounts of stabilizers are added as indicated in the following table. After chemical ripening the emulsion samples are coated onto strips of a support and dried.

After storing these light-sensitive materials in a warm and humid atmosphere they are exposed for 4 sec. and developed for 4 minutes in a solution of the following composition:

	G.
N-methyl-p-aminophenol hemisulphate	1.5
Hydroquinone	6
Sodium sulphite	100
Sodium carbonate	80
Potassium bromide	2
Ethylenediamine tetracetic acid trisodium salt	1.5
Water to make 1 l.	

After further treating this sensitive material in a stop bath, washing and fixing the following comparative results were noted.

Stabilizer	Concentration in mg./mol of silver halide	Fog value		
		Of freshly coated emulsion	After 36 h. of incubation	After 5 days of incubation
	Mg.			
Compound 1.....	60	0.09	0.34	1.22
Compound 1.....	150	0.03	0.06	0.29
Compound 2.....	30	0.04	0.07	0.20
Compound 2.....	150	0.04	0.10	0.73
Compound 4.....	25	0.03	0.04	0.09
Compound 4.....	75	0.05	0.13	0.75
Compound 5.....	30	0.02	0.03	0.12
Compound 5.....	30	0.04	0.09	0.47

These compounds are active not only as stabilizers or as anti-fogging agents, but they also improve the image tone of the developed image, especially in the case the photographic material is hot-glazed. Generally the image thus obtained possesses a bluish black tone without showing, however, a metallic gloss.

Example 2

To a silver bromo-iodide emulsion (3% of iodide) for the enlargement of negatives, 1.5 g. of compound 1 is added per mol of silver halide. This emulsion is coated onto a paper support. After drying, this material is exposed in an exact way and then developed for 2 minutes in a solution as described in Example 1.

After further treatment and hot-glazing, the obtained silver image possesses a neutral bluish, black image tone. If the emulsion does not contain the above compound, the image tone is more bronze-coloured and after hot-glazing, the silver shows a metallic gloss.

Example 3

By replacing in the emulsion of Example 2, 1.5 g. of compound 1 by 3.5 g. of compound 2 and treating as in that example, the same results are obtained.

Example 4

To a silver chloro-bromide emulsion (35% of chloride) suitable for enlarging negatives, 0.7 g. of the compound 3 is added per mol of silver halide. The emulsion is coated onto a paper support.

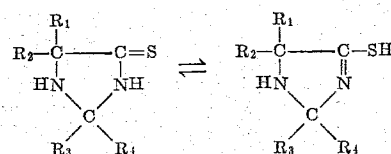
This material is exposed in an exact way and developed for 2 min. in a same solution as described in Example 1. After further treating the material in a stop-bath, washing, fixing, washing and hot-glazing, a silver image is obtained possessing a bluish black image tone without showing any metal gloss or bronzy decoloration. If the emulsion does not contain the above compound, the image tone is more bronze-coloured and after hot-glazing, the silver shows a metallic gloss.

Example 5

By replacing in the emulsion of Example 4, 0.7 g. of compound 3 by 2 g. of compound 1 and treating in the same way as in Example 2, identical results are obtained.

I claim:

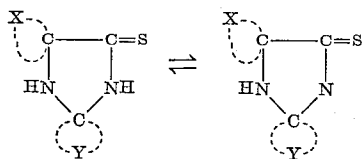
1. Photographic light-sensitive material comprising a silver halide emulsion layer and containing in at least one of its water-permeable layers an imidazolidine-4-thione of the formula:



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wherein each of R_1 , R_2 , R_3 and R_4 is a member selected from the group consisting of a hydrogen atom, an alkyl group and an aryl group.

2. Photographic light-sensitive material comprising a silver halide emulsion layer and containing in at least one of its water-permeable layers an imidazolidine-4-thione of the formula:

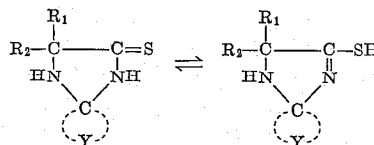


wherein each of X and Y are the necessary atoms to close a saturated cycloaliphatic ring.

3. Photographic light-sensitive material comprising a silver halide emulsion layer and containing in at least one

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of its water-permeable layers an imidazolidine-4-thione of the formula



wherein each of R_1 and R_2 is a member selected from the group consisting of a hydrogen atom, an alkyl group and an aryl group, and

Y represents the necessary atoms to close a saturated cycloaliphatic ring.

References Cited in the file of this patent

Bruenner: Photographic Science and Engineering, vol. 4, No. 4, pages 186-195, July-August 1960.

Futaki et al.: Photographic Science and Engineering, vol. 4, No. 5, pages 257-263, September-October 1960.