

UNITED STATES PATENT OFFICE

2,590,775

SILVER HALIDE EMULSION CONTAINING A
THIO-IMINO-URAZOLE AS A STABILIZERJohn David Kendall and Douglas James Fry,
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Ilford, England, a British companyNo Drawing. Application April 11, 1950, Serial
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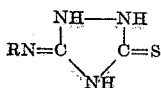
12 Claims. (Cl. 95-7)

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This invention relates to compounds which, when included in a photographic silver halide emulsion layer, or in another layer present in a photographic material including such an emulsion layer, or to the developer, fixer or other processing bath applied to the photographic material, improve the quality of the developed photographic images obtained.

In the production of photographic images in silver halide emulsions, and particularly in the case of emulsions in which the silver halide is predominantly silver chloride, the maximum image density obtainable is not always so great as may be desired. Moreover, the common practice of hot-glazing photographic prints tends to affect adversely the image colour, giving a poor quality black having a "bronzed" appearance, and also reduces the effective maximum density obtainable in the image.

It has now been discovered that this bronzing effect may be reduced or eliminated and the maximum density obtainable may be increased by bringing into contact with the photographic emulsion a member of a certain class of heterocyclic nitrogen compounds, and according to this invention, therefore, a method of improving photographic silver halide emulsions in regard to the quality of the images developed therein comprises applying to such emulsions, e. g. by including in the emulsion, or in another layer of the photographic element containing such emulsion, or in a developing, fixing or other processing bath with which the photographic element is treated, a heterocyclic compound of the general formula:



where R is a hydrogen atom or a hydrocarbon group.

The said compounds may be defined as 3-thio-5-iminourazoles and may be prepared by well known methods. For example the compound in which R is a hydrogen atom may be prepared by the method described in Liebig's Annalen der Chemie, volume 426, at page 313, and the compound where R is a phenyl group may be prepared by the method described in Berichte der Deutschen Chemischen Gesellschaft, volume 55, at page 12. These two compounds are the preferred compounds for use in the present invention, but the invention also includes the use of compounds where R represents other hydrocarbon groups, e. g. alkyl, such as methyl, ethyl and higher alkyl, aralkyl, such as benzyl, and other aryl groups, such as naphthyl.

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The compounds may be used as free bases or as ammonium or alkali metal salts. They may also be used in the form of their substantially water-insoluble colourless metal derivatives, said metal derivatives being soluble or decomposable during treatment of the photographic element with processing baths subsequent to the development of the element. Such metal salts may be silver or nickel or other metal mentioned in British Specification No. 573,745 to which reference is made for details of this aspect of the invention.

As already indicated these compounds may be included in the silver halide photographic emulsion or in another layer of the photographic element, preferably coated adjacent to such emulsion layer, for example in a sub-coat layer or in a super-coat layer. The optimum quantity of compound to be employed will always be small, but will depend on the particular substance selected. In general it is found that for incorporation in an emulsion, sub-coat or super-coat, a proportion of 1 part of the compound in 1000 to 100,000 of the emulsion, super-coat or sub-coat solution is generally suitable, while for incorporation in a developer, fixer or other treatment bath, e. g. a glazing solution, the optimum quantity may be, for example, between 1 part in 3000 to 1 part in 300,000 parts of the processing solution. Frequently even lower concentrations than those given above have some effect and, though it may be uneconomic in being a waste of material, even higher concentrations may be employed.

More than one compound of the type defined may be used if desired, and the compound or compounds may be used in more than one way, e. g. in super-coat and developing solution, or in both developing and fixing solutions.

Mixtures of the compounds with any of those specified for similar use in British Specifications Nos. 573,745 and 583,648 may also be employed.

In general the compounds will be applied to the photographic emulsion before reaching the final stage of drying the developed image, but they may be applied with advantage to already dried prints where it is desired to subject the latter to hot-glazing.

The following examples illustrate the invention:

Example 1

To a gelatin super-coat solution was added a solution of 3-thio-5-iminourazole in the proportion of 1 part of the compound per 5000 parts of the gelatin solution by weight. This super-coat was applied over—

(A) A silver chloride photographic emulsion of the type known as "vigorous gaslight."

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(B) A silver bromide photographic emulsion of the type used for vigorous bromide printing paper, each of said emulsions being coated on paper base. A comparative test (control) was made with plain gelatin super-coat.

Test strips of the papers thus obtained were exposed, developed, fixed, washed, and some specimens cold-dried and others hot-glazed. The examination of the papers gave the following results:

Emulsion (A or B)	Maximum density of cold-dried coatings	Maximum density after hot glazing
Control A.....	1.84	1.50
Test A.....	1.87	1.95
Control B.....	1.90	1.65
Test B.....	1.94	2.01

Example 2

A silver chloride photographic printing paper of the type known as "vigorous gaslight" was exposed and developed in a standard metol-hydroquinone developer, fixed, washed and hot-glazed. Small quantities of 3-thio-5-phenyliminourazole were added to the developing bath and, in a second test, to the acid fixing bath, and the following results were obtained.

Test	Developer addition	Fixing bath addition	Maximum density after hot-glazing
Control.....	None.....	None.....	1.41
A.....	1 part per 1,000.	do.....	2.02
B.....	None.....	One part per 10,000.	1.76

What we claim is:

1. A method of improving photographic silver halide emulsions in regard to the quality of the images developed therein which comprises developing such emulsions in a developing bath which contains a small quantity of 3-thio-5-phenyliminourazole.

2. A method of improving photographic silver halide emulsions in regard to the quality of the images developed therein which comprises developing such emulsions in a developing bath which contains a small quantity of 3-thio-5-iminourazole.

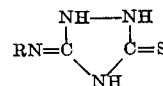
3. A method of improving photographic silver halide emulsions in regard to the quality of the images developed therein which comprises developing such emulsions and thereafter fixing the emulsions in a fixing bath containing a small quantity of 3-thio-5-phenyliminourazole.

4. A method of improving photographic silver halide emulsions in regard to the quality of the images developed therein which comprises developing such emulsions and thereafter fixing the emulsions in a fixing bath containing a small quantity of 3-thio-5-iminourazole.

5. A photographic element which includes a silver halide photographic emulsion layer and

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in contact therewith uniformly throughout, a small quantity of a heterocyclic compound of the general formula:



where R is selected from the class consisting of the hydrogen atom and hydrocarbon groups.

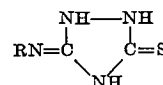
6. A photographic element which includes a silver halide photographic emulsion layer and in contact therewith uniformly throughout, a small quantity of 3-thio-5-phenyliminourazole.

7. A photographic element which includes a silver halide photographic emulsion layer and in contact therewith uniformly throughout, a small quantity of 3-thio-5-iminourazole.

8. A photographic element which comprises a silver halide photographic emulsion layer and coated adjacent thereto a water-permeable colloid layer which contains a small proportion of 3-thio-5-phenyliminourazole.

9. A photographic element which comprises a silver halide photographic emulsion layer and coated adjacent thereto a water-permeable colloid layer which contains a small proportion of 3-thio-5-iminourazole.

10. A method of improving photographic silver halide emulsions in regard to the quality of the images developed therein which comprises treating such emulsions with photographic processing baths in the presence, at least at one stage in the processing, of a heterocyclic compound of the general formula:



where R is selected from the class consisting of the hydrogen atom and hydrocarbon groups.

11. A method of improving photographic silver halide emulsions in regard to the quality of the images developed therein which comprises treating such emulsions with photographic processing baths in the presence, at least at one stage in the processing, of a small quantity of 3-thio-5-phenyliminourazole.

12. A method of improving photographic silver halide emulsions in regard to the quality of the images developed therein which comprises treating such emulsions with photographic processing baths in the presence, at least at one stage in the processing, of a small quantity of 3-thio-5-iminourazole.

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