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TREATMENT OF DEVELOPED SILVER IMAGES WITH MERCAPTO-TETRAZOLE AND TRIAZOLE COMPOUNDS

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This invention relates to compounds which serve as improvers for photographic silver halide emulsions and particularly to compounds which, when applied to the emulsion subsequent to the development of a photographic image therein, improve the quality of the photographic image obtained.

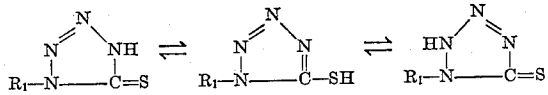
It has now been discovered that 5-mercapto-tetrazoles, 5-mercapto-1.2.4-triazoles, and soluble salts thereof, when applied to a photographic silver halide emulsion after a silver image has been developed therein have a very valuable effect in that these compounds permit photographic silver images to be obtained which have a greater maximum density than is obtained in the absence of the compounds, and also prevent or reduce the "bronzing" effect commonly obtained when photographic silver images are hot-glazed. These results are remarkable since it might reasonably have been supposed that any attempt to modify the maximum density of the image would have to be effective during the development of the image. Many proposals have, in fact, been made for improving the quality of the developed image by adding compounds to the photographic emulsion or developer, but these additions have generally also resulted in a loss in speed of the emulsion. In the present invention, however, the compounds are not added until after development and the speed of the emulsion is therefore unaffected.

According to the present invention, therefore, a method of improving the quality of a silver image developed in a photographic silver halide emulsion comprises treating the developed image, after its removal from the developing bath, with a 5-mercapto-tetrazole or a 5-mercapto-1.2.4-triazole, or a soluble salt of either of such compounds.

The mercapto-tetrazole or mercapto-triazole may be applied to the developed image as an aqueous solution immediately following development, or the compound may be included in the fixing bath, or may be applied as an aqueous solution after fixing. Where the photographic images are to be glazed the compound may be added to a glazing solution if such is used. In general the compounds will be applied to the photographic image before the latter is dried, but they may be applied with advantage to an already dried print where it is desired to subject the latter to hot-glazing.

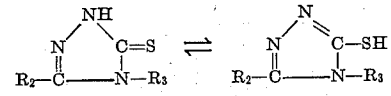
The 5-mercapto tetrazole may be any compound of the tautomeric formulae:

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where R_1 is a hydrogen atom or a hydrocarbon substituent group (which may itself be substituted or unsubstituted). The hydrocarbon substituent, where present, may be an alkyl, aralkyl or aryl group or a substituted group of this type, e. g. a methyl, ethyl or higher alkyl group or an unsaturated group of this type (as for instance an allyl group), a benzyl group, a cycloalkyl group (as for instance a cyclohexyl group), or a phenyl or naphthyl group which may be substituted (as for instance a β-naphthyl group, a p-diethyl-amino - phenyl group, an o-methoxy - phenyl group, or a p-chlor-phenyl group).

The 5-mercapto-1.2.4-triazole may be any compound of the tautomeric formulae:



where R_2 and R_3 are the same or different and are hydrogen atoms or hydrocarbon groups. Where either R_2 and R_3 or both is a hydrocarbon group it can be any of those referred to above in connection with R_1. Examples of compounds of this type are:

3:4-dimethyl-5-mercapto-1.2.4-triazole
3-methyl-4-ethyl-5-mercapto-1.2.4-triazole
3-methyl-4-phenyl-5-mercapto-1.2.4-triazole
4-phenyl-5-mercapto-1.2.4-triazole
4-benzyl-5-mercapto-1.2.4-triazole
3-ethyl-4-methyl-5-mercapto-1.2.4-triazole
3-n-hexyl-4-methyl-5-mercapto-1.2.4-triazole
3-methyl-4-p-hydroxyphenyl-5-mercapto - 1.2.4-triazole
3-methyl - 4 - p-aminophenyl-5-mercapto-1.2.4-triazole
3-phenyl - 4-α - naphthyl-5-mercapto - 1.2.4-triazole
3-α-naphthyl-5-mercapto-1.2.4-triazole
3.4-diphenyl-5-mercapto-1.2.4-triazole

Only very small quantities of the mercapto-tetrazole or mercapto-triazole or soluble salts thereof are necessary to produce a satisfactory improvement in the quality of the photographic image. A treatment solution containing 1 part of the compound in 10,000 parts of water is satisfactory, though lower or higher concentrations may be used, for example 1 part in 3,000 to 1 part in 300,000 parts of water. Similar concentrations of compound are suitable in fixing or

glazing solutions. The optimum concentration in any particular case will depend on the particular compound used and on the degree of the effect required. Even lower concentrations than those given above yield some effect and, though it may be uneconomic in being a waste of material, higher concentrations can also be employed.

Conveniently the mercapto compounds may be brought into solution by dissolving them in a small quantity of dilute sodium carbonate and then diluting to the desired concentration by adding the solution to water, fixing bath or glazing solution. In some cases the mercapto compounds are soluble in water and in others they are relatively insoluble even in dilute sodium carbonate solution. In this latter case the compounds may conveniently be dissolved in ethyl alcohol and the alcohol solution then diluted by addition to water, fixing bath or glazing solution.

The following examples illustrate the invention:

EXAMPLE 1

Addition of the Compounds to a Fixing Solution

Test samples of photographic printing paper carrying an emulsion consisting essentially of silver chloride were exposed and developed in the usual way. After development the samples were given a quick rinse in plain water and then transferred to one of a series of fixing baths formulated as follows:

Sodium thiosulphate	grams	200
Potassium metabisulphite	do	25
Water to make	ccs	1,000

To each bath of the series was added a proportion of a mercapto compound according to the invention, such that the mercapto compound was present approximately in the proportion of 1 part in 10,000 of the fixing solution.

After fixation was complete (about 10 minutes) the samples were well washed.

Of the samples treated with each different fixing solution one was dried normally in air, one was cold-glazed and one was hot-glazed on a commercial hot-glazing machine. The resulting photographic images were examined to determine the maximum density of the image (D_{max}) and were examined visually to judge the extent of "bronzing," if any, of the image. The D_{max} values obtained were as set out in the following Table I:

Table I

Compound	Normally dried	Cold Glazed	Hot Glazed
None (control)	1.79	1.74	1.53
5-mercapto-1.2.4-triazole	1.93	1.95	2.05
3.4-dimethyl-5-mercapto-1.2.4-triazole	1.95	1.95	1.92
3-methyl-4-ethyl-5-mercapto-1.2.4-triazole	1.90	1.96	1.97
3-methyl-4-phenyl-5-mercapto-1.2.4-triazole	1.90	1.93	2.06
4-benzyl-5-mercapto-1.2.4-triazole	1.94	1.96	2.05
3-ethyl-4-methyl-5-mercapto-1.2.4-triazole	1.91	1.92	1.93
3-n-hexyl-4-mercapto-1.2.4-triazole	1.97	1.97	2.07
1-phenyl-5-mercapto-tetrazole	1.90	1.93	2.05
1-methyl-5-mercapto-tetrazole	1.90	1.92	1.76
1-α-naphthyl-5-mercapto-tetrazole	1.90	1.92	2.07
1-cyclohexyl-5-mercapto-tetrazole	1.94	1.97	2.07
5-mercapto-tetrazole	1.85	1.86	2.06
1-benzyl-5-mercapto-tetrazole	1.92	1.93	2.04

It will be apparent from the above table that a very considerable increase in D_{max} was obtained in all cases. Moreover, in all cases the degree of bronzing of the image on hot-glazing was, compared with the control sample, very much reduced.

EXAMPLE 2

The procedure of Example I was followed using a photographic paper carrying an emulsion consisting essentially of silver bromide and the resulting photographic prints were hot-glazed on a commercial hot-glazing machine. D_{max} values were determined and found to be as set out in the following Table II:

Table II

Compound	D_{max}
None (control)	1.80
5-mercapto-1.2.4-triazole	2.08
3.4-dimethyl-5-mercapto-1.2.4-triazole	2.02
3-methyl-4-ethyl-5-mercapto-1.2.4-triazole	2.05
3-methyl-4-phenyl-5-mercapto-1.2.4-triazole	2.07
4-benzyl-5-mercapto-1.2.4-triazole	2.08
3-ethyl-4-methyl-5-mercapto-1.2.4-triazole	2.03
3-n-hexyl-4-methyl-5-mercapto-1.2.4-triazole	2.00
1-phenyl-5-mercapto tetrazole	2.04
1-methyl-5-mercapto tetrazole	2.02
1-α-naphthyl-5-mercapto tetrazole	2.07
1-cyclohexyl-5-mercapto tetrazole	2.05
5-mercapto tetrazole	2.08
1-benzyl-5-mercapto-tetrazole	2.06

In addition to the increase in D_{max} obtained in all cases, there was a marked decrease in the degree of bronzing as compared with the control sample.

EXAMPLE 3

Addition of the Compounds to a Glazing Solution

The procedure of Examples 1 and 2 was followed using both the stated types of paper. The fixing solution was used without any addition of mercapto compound and the washed sample strips were bathed in a glazing solution consisting of:

10% aqueous formaldehyde	cubic centimeters	100
Ethyl alcohol	do	40
Water to make	do	1000

to which was added 1 part in 10,000 of the mercapto compound. The strips were then hot-glazed on a commercial hot-glazing machine. D_{max} values were determined as before with the results shown in the following Table III:

Table III

Compound	Paper Carrving Emulsion of Example 1	Paper Carrying Emulsion of Example 2
None (control)	1.49	1.74
5-mercapto-1.2.4-triazole	1.82	2.04
3.4-dimethyl-5-mercapto-1.2.4-triazole	1.83	1.99
3-methyl-4-ethyl-5-mercapto-1.2.4-triazole	1.82	1.99
3-methyl-4-phenyl-5-mercapto 1.2.4-triazole	1.85	2.02
4-benzyl-5-mercapto-1.2.4-triazole	1.83	2.02
3-ethyl-4-methyl-5-mercapto-1.2.4-triazole	1.80	1.99
3-n-hexyl-4-methyl 5-mercapto-1.2.4-triazole	1.84	2.05
1-phenyl-5-mercapto-tetrazole	1.86	2.02
1-methyl-5-mercapto-tetrazole	1.71	1.95
1-α-naphthyl-5-mercapto-tetrazole	1.85	2.04
1-cyclohexyl-5-mercapto-tetrazole	1.76	2.03
5-mercapto-tetrazole	1.85	2.02
1-benzyl-5-mercapto-tetrazole	1.77	2.02

In addition to the general improvement in D_{max} shown by the figures in the foregoing table, the compounds gave a marked improvement in the quality of the image in that whereas the control sample was badly bronzed on hot-glazing, the degree of bronzing was very much reduced or

even eliminated in the case of the samples treated with the mercapto compounds.

EXAMPLE 4

An already dried (but unglazed) print on a silver chloride printing paper was re-wetted and hot-glazed on a commercial hot-glazing machine. The resulting image had D_{max} value of 1.54. A similar dried print was re-wetted, bathed in a 1 in 10,000 solution of 1-phenyl-5-mercapto tetrazole, and hot-glazed as before. The resulting image had D_{max} value of 1.90.

What we claim is:

1. A method of improving the quality of a silver image developed in a photographic silver halide emulsion which comprises treating the developed image, after its removal from the developing bath, with a compound selected from the group consisting of tautomeric unsubstituted and mono-N-hydrocarbon substituted 5-mercapto-tetrazoles, tautomeric unsubstituted and mono- and di-hydrocarbon substituted 5-mercapto-1.2.4-triazoles in which the 1-position is unsubstituted and any hydrocarbon substituents are in the 3- and 4-positions, and soluble salts of such compounds.

2. A method of improving the quality of a silver image developed in a photographic gelatin silver halide emulsion which comprises treating the developed image, after its removal from the developing bath, with a compound selected from the group consisting of tautomeric unsubstituted and mono-N-hydrocarbon substituted 5-mercapto - tetrazoles, tautomeric unsubstituted and mono- and di-hydrocarbon substituted 5-mercapto-1.2.4-triazoles in which the 1-position is unsubstituted and any hydrocarbon substituents are in the 3- and 4-positions, and soluble salts of such compounds.

3. A method of improving the quality of a silver image developed in a photographic gelatin silver halide emulsion which comprises treating the developed image, immediately after its development, with an aqueous solution of a compound selected from the group consisting of tautomeric unsubstituted and mono-N-hydrocarbon substituted 5-mercapto-tetrazoles, tautomeric unsubstituted and mono- and di-hydrocarbon substituted 5-mercapto-1.2.4-triazoles in which the 1-position is unsubstituted and any hydrocarbon substituents are in the 3- and 4-positions, and soluble salts of such compounds.

4. A method of improving the quality of a silver image developed in a photographic gelatin silver halide emulsion which comprises treating the developed image, after its development, with a fixing solution containing a compound selected from the group consisting of tautomeric unsubstituted and mono-N-hydrocarbon substituted 5-mercapto-tetrazoles, tautomeric unsubstituted and mono- and di-hydrocarbon substituted 5-mercapto-1.2.4-triazoles in which the 1-position is unsubstituted and any hydrocarbon substituents are in the 3- and 4-positions, and soluble salts of such compounds.

5. A method of improving the quality of a silver image developed in a photographic gelatin silver halide emulsion which comprises treating the developed image, after its development and fixation, with an aqueous solution of a compound selected from the group consisting of tautomeric unsubstituted and mono-N-hydrocarbon substituted 5-mercapto-tetrazoles, tautomeric unsubstituted and mono- and di-hydrocarbon substituted 5-mercapto-1.2.4-triazoles in which the 1-position is unsubstituted and any hydrocarbon substituents are in the 3- and 4-positions, and soluble salts of such compounds.

6. A method of improving the quality of a silver image developed in a photographic gelatin silver halide emulsion which comprises treating the developed image, after its development and fixation, with a glazing solution containing a compound selected from the group consisting of tautomeric unsubstituted and mono-N-hydrocarbon substituted 5-mercapto-tetrazoles, tautomeric unsubstituted and mono- and di-hydrocarbon substituted 5-mercapto-1.2.4-triazoles in which the 1-position is unsubstituted and any hydrocarbon substituents are in the 3- and 4-positions, and soluble salts of such compounds, and thereafter drying and glazing the said image.

7. A method of improving the quality of a silver image developed in a photographic gelatin silver halide emulsion which comprises treating the developed image, after its development and fixation, with a glazing solution containing a compound selected from the group consisting of tautomeric unsubstituted and mono-N-hydrocarbon substituted 5-mercapto-tetrazoles, tautomeric unsubstituted and mono- and di-hydrocarbon substituted 5-mercapto-1.2.4-triazoles in which the 1-position is unsubstituted and any hydrocarbon substituents are in the 3- and 4-positions, and soluble salts of such compounds, and thereafter drying and hot-glazing the said image.

8. A method of improving the quality of a silver image developed in a photographic gelatin silver halide emulsion which comprises treating the developed image, after it has been fixed and dried, with an aqueous solution of a compound selected from the group consisting of tautomeric unsubstituted and mono-N-hydrocarbon substituted 5-mercapto-tetrazoles, tautomeric unsubstituted and mono- and di-hydrocarbon substituted 5-mercapto-1.2.4-triazoles in which the 1-position is unsubstituted and any hydrocarbon substituents are in the 3- and 4-positions, and soluble salts of such compounds, and thereafter re-drying and glazing the said image.

9. A method of improving the quality of a silver image developed in a photographic gelatin silver halide emulsion which comprises treating the developed image, after it has been fixed and dried, with an aqueous solution of a compound selected from the group consisting of tautomeric unsubstituted and mono-N-hydrocarbon substituted 5-mercapto-tetrazoles, tautomeric unsubstituted and mono- and di-hydrocarbon substituted 5-mercapto-1.2.4-triazoles in which the 1-position is unsubstituted and any hydrocarbon substitutents are in the 3- and 4-positions, and soluble salts of such compounds, and thereafter re-drying and hot-glazing the said image.

10. A method of improving the quality of a silver image developed in a photographic gelatin silver halide emulsion which comprises treating the developed image, after its removal from the developing bath, with a 5-mercapto-1.2.4-triazole compound which is unsubstituted in the 1-position and contains a substituent in the 3- and 4-positions taken from the class consisting of hydrogen and hydrocarbon radicals, said compound containing at least one hydrocarbon radical in said latter positions.

11. A method of improving the quality of a silver image developed in a photographic gelatin silver halide emulsion which comprises treating the developed image, after its removal from the developing bath, with a 5-mercapto-tetrazole

compound containing a hydrocarbon substituent group in the 1-position.

12. A method of improving the quality of a silver image developed in a photographic gelatin silver halide emulsion which comprises treating the developed image, after its removal from the developing bath, with a 5-mercapto-tetrazole compound containing an aryl substituent group in the 1-position.

13. A method of improving the quality of a silver image developed in a photographic silver halide emulsion coated on a paper base, which comprises treating the developed image, after its removal from the developing bath, with a fixing solution containing a compound selected from the group consisting of tautomeric unsubstituted and mono-N-hydrocarbon substituted 5-mercapto-tetrazoles, tautomeric unsubstituted and mono- and di-hydrocarbon substituted 5-mercapto-1.2.4-triazoles in which the 1-position is unsubstituted and any hydrocarbon substituents are in the 3- and 4-positions, and soluble salts of such compounds.

14. Photographic fixing solutions containing a small quantity of a compound selected from the group consisting of tautomeric unsubstituted and mono-N-hydrocarbon substituted 5-mercapto-tetrazoles, tautomeric unsubstituted and mono- and di-hydrocarbon substituted 5-mercapto-1.2.4-triazoles in which the 1-position is unsubstituted and any hydrocarbon substituents are in the 3- and 4-positions, and soluble salts of such compounds.

15. Photographic glazing solutions containing a small quantity of a compound selected from the group consisting of tautomeric unsubstituted and mono-N-hydrocarbon substituted 5-mercapto-tetrazoles, tautomeric unsubstituted and mono- and di-hydrocarbon substituted 5-mercapto-1.2.4-triazoles in which the 1-position is unsubstituted and any hydrocarbon substituents are in the 3- and 4-positions, and soluble salts of such compounds.

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