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PHOTOGRAPHIC ANTIPLUMMING AGENTS AND COMPOSITIONS CONTAINING THEM

Edward B. Knott and Philip K. Brooks, Harrow, England, assignors to Eastman Kodak Company, Rochester, N. Y., a corporation of New Jersey

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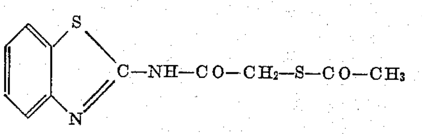
9 Claims. (Cl. 95—7)

This invention relates to improvements in the production of photographic images, especially images on paper supports prepared from silver halide emulsions.

Silver halide emulsions are frequently subject to image degradation during processing, that is, during development, fixing, washing, toning, or other treatment and during the moist heat to which they are subjected on drying, as when prints are subjected to ferrotyping or hot-type glazing. This degradation of the image frequently manifests itself as "plumming" or "bronzing" of the image.

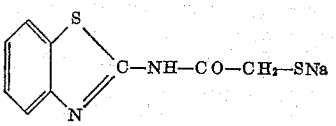
It is known that 2-acetylthioglycolamidobenzthiazole having the following formula:

I.



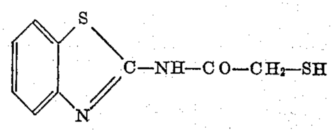
can be employed as an anti-plumming agent for photographic silver halide emulsions. Moreover, the alkaline hydrolysis product of the above compound:

II.



is an efficient anti-plumming agent. Attempts to isolate the free thiol:

III.

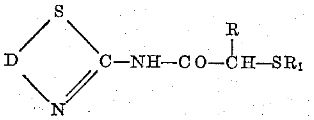


from the alkaline hydrolysis mixture usually result in isomerization to a difficultly soluble product which is unsuitable as an addition agent for photographic emulsions. It is suitable to prepare an alkaline hydrolysate of compound I and add the freshly prepared hydrolysate to a photographic emulsion. Such an alkaline hydrolysate is not stable and develops an orange colour and sediment upon standing. Moreover, such hydrolysates become increasingly powerful desensitizers upon standing. It is essential, therefore, to add such hydrolysates to photographic emulsions as soon as possible after preparation.

We have now found, however, that compounds

which can be represented by the following general formula:

IV.

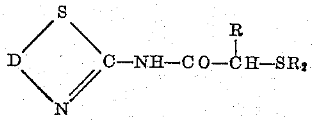


wherein D represents an arylene group, e. g. o-phenylene, o-naphthylene, etc., which may be unsubstituted or substituted, for example, with an alkyl (e. g. methyl, ethyl, etc.) and/or alkoxyl (e. g. methoxy, ethoxy, etc.) group, R represents an alkyl group, e. g. methyl, ethyl, etc. and R_1 represents an acyl group, e. g. acetyl, propionyl, etc. can be hydrolyzed in alkaline media to give hydrolysates which not only are effective anti-plumming agents, but which, upon prolonged standing, develop only a faint yellow colour and show no increase in desensitizing properties.

It is, therefore, an object of our invention to provide a means for preventing image degradation in an exposed silver halide emulsion. Still another object is to provide new chemical compounds. Another object is to provide a method for making these new compounds. Another object is to provide photographic silver halide emulsions containing these new compounds. Other objects will become apparent from a consideration of the following examples and description.

Accordingly, the present invention provides a method of preventing image degradation of an exposed silver halide emulsion during processing which comprises performing one or more of the steps of developing, fixing, washing and drying an exposed silver halide emulsion in the presence of one or more compounds represented by the following general formula:

V.

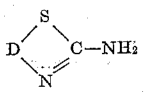


wherein D represents an arylene group, e. g. o-phenylene, o-naphthylene, etc., which may be unsubstituted or substituted, for example, with alkyl (e. g. methyl, ethyl, etc.) and/or alkoxyl (e. g. methoxy, ethoxy, etc.) groups, R represents an alkyl group, e. g. methyl, ethyl, etc., and R_2 represents a hydrogen atom or a metallic atom, such as a sodium atom, potassium atom or other alkali metal atom.

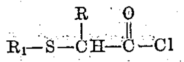
When any of the above compounds represented by Formula V are incorporated in silver halide emulsions, these compounds are advantageously used in a gelatino-silver-chloride emulsion or a silver chloride emulsion containing small amounts of bromide or iodide. Silver halide emulsions in which the carrier is polyvinyl alcohol or hydrolyzed cellulose acetate can also be used. When the compounds are incorporated in the emulsion, they should be used in amounts of from 2.5 to 25 grams per unit of silver halide formed from 1000 grams of silver nitrate. The same concentration of the compounds should be present in the emulsion when the compounds are added by bathing the emulsion in a solution containing them. When the emulsion layer is bathed in a solution of the compound, the solution may contain up to about 5% by weight of the compound.

The compounds of Formula IV can be prepared by condensing an amino compound selected from those represented by the following general formula:

VI.



with an acid chloride selected from those represented by the following general formula:



$$R_1-S-\overset{\overset{R}{|}}{C}H-\overset{\overset{O}{\|}}{C}-Cl$$

wherein R and R_1 each have the values given above, in the presence of an acid-binding agent, e. g. a tertiary amine. The resulting acyl compounds can be hydrolyzed, in the presence of an alkali metal hydroxide (e. g. sodium hydroxide, etc.), to give compounds of Formula V wherein R_2 represents a metallic atom. Such metal salts can be converted with acid (e. g. sulfuric, hydrochloric, etc.) to the free thiol (where R_2 in Formula V represents a hydrogen atom).

The invention will be clearly understood from the following example, which is given by way of illustration only.

EXAMPLE

The following table shows the improvement of an alkaline hydrolysate of a compound represented by Formula IV above (2-α-acetylthiopropionamido-6-ethoxybenzothiazole) over the alkaline hydrolysate of 2-acetylthioglycolamidobenzothiazole when the alkaline hydrolysates are added to a photographic silver halide emulsion immediately after preparation and after standing for various periods.

TABLE

alkaline hydrolysate of—	Speed (D=0.5 above fog)			
	Freshly prepared	after 2 days' standing	after 5 days' standing	after 14 days' standing
A. none	525	537	490	575
B. 2-acetylthioglycolamidobenzothiazole	347	117	34.7	25.7
C. 2-α-acetylthiopropionamido-6-ethoxybenzothiazole	389	390	380	436

In the foregoing table the amount of hydrolyzed material (sodium 2-thioglycolamidobenzothiazole) under B and sodium 2-α-mercaptopropionamido-6-ethoxybenzothiazole under C employed in the photographic silver halide emulsion was 5 g. per unit of silver halide formed from 1000 g. of silver nitrate.

The following examples will serve to illustrate the preparation of the acyl, metal salt and free thio compounds of the invention:

Example 1.—2-α-acetylthiopropionamido-6-ethoxybenzthiazole

2-α-amino-6-ethoxybenzthiazole (19.4 g.) was dissolved in dioxane (100 cc.) by warming. Quinoline (12.8 g.) was added and α-acetylthiopropionylchloride (17 g.) dripped in with stirring at 23° C. After the addition the mixture was stirred 2 hours and poured into water (750 cc.). An oil separated which slowly crystallized. From ethanol (50 cc.), it formed almost colourless leaflets M. P. 118° C. (9.5 g.).

Example 2.—2-α-mercaptopropionamido-6-ethoxybenzthiazole

2 - α - acetylthiopropionamido - 6-ethoxybenzthiazole (3.25 g.) was dissolved in acetone (25 cc.). A solution of sodium hydroxide (0.8 g.) in water (25 cc.) was added at 25° C. The temperature rose to 30° C. Water (100 cc.) was added and the solution filtered. This solution can be used for photographic purposes as described above. On adding 2N hydrochloric acid (10 cc.) the required thiol separated. From benzene it formed fine crystals M. P. 145°–148° C.

The 2-acetylthiopropionyl chloride used in Example 1 was prepared as shown in the following example:

Example 3.—α-Acetylthiopropionylchloride

α-Acetylthiopropionic acid (67 g.) was placed in 500 cc. three-necked flask fitted with stirrer, condenser and dropping funnel and thionylchloride (61 cc.) run in at such a rate that the temperature did not exceed 25° C. It was then stirred overnight, the solvent removed at 60°–70° C./20 mm. and the acid chloride collected at 58°–62° C./1 mm. Yield 17 g.

The α-acetylthiopropionic acid used in Example 3 can be prepared by the method of Neuberger, Biochem. J. 1938, 36, 1452, or as shown in the following example:

Example 4.—α-Acetylthiopropionic acid

α-Mercaptopropionic acid (98 g.) was placed in a 500 cc. three-necked flask fitted with stirrer, condenser and dropping funnel. Acetylchloride (120 cc.) was slowly dripped in with stirring. When the addition was complete the mixture was stirred 5 minutes longer and distilled. The fraction B. P. 120°–128° C./9 mm. was collected (67 g.).

Example 5.—2-α-mercaptopropionamidobenzthiazole

2-aminobenzthiazole (10.6 g.) was dissolved in dioxane (70 cc.) with warming. Quinoline (9.2 g.) was added and with stirring α-acetylthiopropionyl chloride (12.0 g.) dripped in over 10 minutes. The mixture was set aside for 2 hours and poured into water to precipitate a yellow oil. The latter was taken up in chloroform, dried with sodium sulphate and the solvent removed. The residual yellow oil was dissolved in ethanol (50 cc.) and at 20° C. a solution of sodium hydroxide (6.0 g.) in water (250 cc.) added all at once. The turbid solution was diluted with water (250 cc.) after 2 minutes, the cloudiness ethered out and the clear aqueous layer acidified. A creamy yellow solid separated. It was collected, washed with water and vacuum dried. Yield 8.0 g., 47.5%. From benzene (twice) it formed cream aggregates, M. P. 161–162° C.

Example 6.—2-α-mercaptopropionamido-6-methoxybenzthiazole

2-amino-6-methoxybenzthiazole (13.0 g.) was dissolved in dioxane (70 cc.), quinoline (9.2 g.) added, and α-acetylthiopropionylchloride (12.0 g.) dripped in with stirring over 10 minutes. The brown oil obtained as above was hydrolysed similarly to give 9.5 g., 49% of the required product which formed buff aggregates, M. P. 156–157° C. from benzene.

Example 7.—6-chloro-2-α-mercaptopropionamidobenzthiazole

To 2-amino-6-chlorobenzthiazole (6.7 g.) in dioxane (30 cc.) was added quinoline (4.7 g.), then α-acetylthiopropionyl chloride (6.0 g.). After 2 hours' standing water (150 cc.) was added to give an oil. This was hydrolysed in ethanol (25 cc.) by adding a solution of sodium hydroxide (3.5 g.) in water (125 cc.). The solid obtained on acidification formed a cream microcrystalline powder, M. P. 183–186° C. from benzene.

Example 8.—2-α-mercaptobutyramidobenzthiazole

2-aminobenzthiazole (7.5 g.) was dissolved in dioxane (50 cc.) by warming, quinoline (6.5 g.) was added, and stirring rapidly, α-acetylthiobutyryl chloride (9.0 g.) dripped in over 10 minutes at 25° C. Quinoline hydrochloride separated rapidly. After completed addition the mixture was stirred for 2 hours and poured into water (250 cc.). A thick yellow oil was precipitated. It was taken up in chloroform and the solvent distilled off. The residual oil was dissolved in ethanol (50 cc.) and a solution of sodium hydroxide (6.0 g.) in water (250 cc.) added at 25° C. After 2 minutes water (250 cc.) was added, the liquor clarified by ether extraction and the required thiol precipitated as a semi-solid with dilute hydrochloric acid. This was washed by decantation, redissolved in 0.5N-sodium hydroxide, clarified by ether extraction and precipitated as a hard solid by acidification. It was collected, washed with water and air dried. From benzene it formed cream needles, M. P. 142–146° C.

The α-acetylthiobutyryl chloride used in Example 8 was prepared as shown in the following example:

Example 9.—α-Acetylbutyrylchloride

α-Acetylthiobutyric acid (73 g.) was treated at 20–25° C. with thionyl chloride (67.4 g.), stood overnight, excess thionyl chloride distilled off at 60–65° C. under reduced pressure (20 mm.) and the oil distilled from the steam bath at 70–72 C./9 mm.

The α-acetylthiobutyric acid used in Example 9 was prepared as shown in the following example:

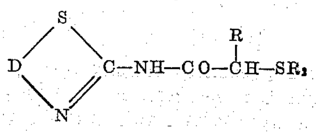
Example 10.—α-Acetylthiobutyric acid

α-Mercaptobutyric acid (52 g.) was placed in a 250 cc. 3-necked flask fitted with stirrer and dropping funnel and acetic anhydride (75 cc.) run in over 10 minutes at room temperature. It was stirred for 5 minutes, then the solvent removed under reduced pressure on the steam bath. The oil was then fractionated, collected at 100–150° C./8 mm. then redistilled and collected (37 g.) at 143–149° C./8 mm.

Other compounds represented by Formula V above can also be used effectively according to our invention.

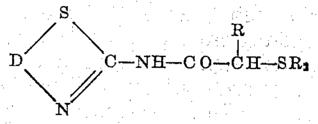
What we claim as our invention and desire secured by Letters Patent of the United States is:

1. The method of preventing image degradation of an exposed silver halide emulsion during processing, which comprises performing at least one of the steps of developing, fixing, washing and drying said emulsion in the presence in said emulsion of from 2.5 grams to 25 grams per unit of silver halide formed from 1000 grams of silver nitrate, of a compound selected from those represented by the following general formula:



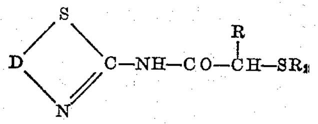
wherein R represents an alkyl group, R_2 represents a member selected from the group consisting of a hydrogen atom and an alkali metal atom, and D represents an arylene group.

2. The method of preventing image degradation of an exposed silver halide emulsion during processing, which comprises performing at least one of the steps of developing, fixing, washing and drying said emulsion in the presence in said emulsion of from 2.5 grams to 25 grams per unit of silver halide formed from 1000 grams of silver nitrate, of a compound selected from those represented by the following general formula:



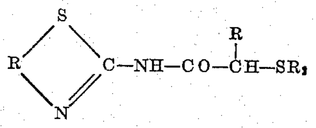
wherein R represents an alkyl group containing from 1 to 2 carbon atoms, R_2 represents a member selected from the group consisting of a hydrogen atom and an alkali metal atom, and D represents a phenylene group.

3. The method of preventing image degradation of an exposed silver halide emulsion during processing, which comprises incorporating in at least one of the developing, fixing and washing baths used to process said emulsion, an appreciable amount but not more than 5%, of a compound selected from those represented by the following general formula:



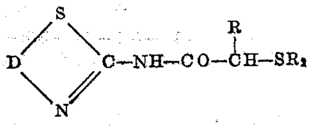
wherein R represents an alkyl group, R_2 represents a member selected from the group consisting of a hydrogen atom and an alkali metal atom, and processing said exposed emulsion in said bath.

4. The method of preventing image degradation of an exposed silver halide emulsion during processing, which comprises incorporating in at least one of the developing, fixing and washing baths used to process said emulsion, an appreciable amount but not more than 5%, of a compound selected from those represented by the following general formula:



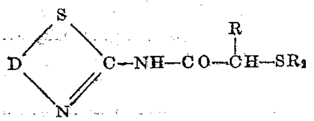
wherein R represents an alkyl group containing from 1 to 2 carbon atoms, R_2 represents a member selected from the group consisting of a hydrogen atom and an alkali metal atom, and D represents a phenylene group, and processing said exposed emulsion in said bath.

5. A photographic silver halide emulsion containing from 2.5 to 25 grams per unit of silver halide formed from 1000 grams of silver nitrate, of a compound selected from those represented by the following general formula:



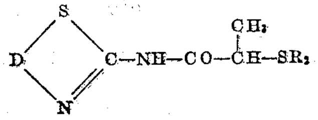
wherein R represents an alkyl group, R_2 represents a member selected from the group consisting of a hydrogen atom and an alkali metal atom, and D represents an arylene group.

6. A photographic silver halide emulsion containing from 2.5 to 25 grams per unit of silver halide formed from 1000 grams of silver nitrate, of a compound selected from those represented by the following general formula:



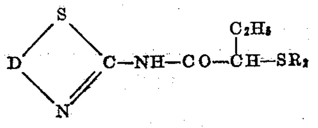
wherein R represents an alkyl group containing from 1 to 2 carbon atoms, R_2 represents a member selected from the group consisting of a hydrogen atom and an alkali metal atom, and D represents a phenylene group.

7. A photographic silver halide emulsion containing from 2.5 to 25 grams per unit of silver halide formed from 1000 grams of silver nitrate, of a compound selected from those represented by the following general formula:



wherein R_2 represents a member selected from the group consisting of a hydrogen atom and D represents an arylene group.

8. A photographic silver halide emulsion containing from 2.5 to 25 grams per unit of silver halide formed from 1000 grams of silver nitrate, of a compound selected from those represented by the following general formula:



wherein R_2 represents a member selected from the group consisting of a hydrogen atom and D represents an arylene group.

9. A photographic silver halide emulsion containing from 2.5 grams per unit to 25 grams per unit of silver halide formed from 1000 grams of silver nitrate, of a compound selected from the group consisting of 2-α-mercaptopropionamidobenzthiazole, 2-α-mercaptopropionamido-6-ethoxybenzthiazole, 2-α-mercaptopropionamido-6-methoxybenzthiazole, 6-chloro-2-α-mercaptopropionamidobenzthiazole, 2-α-mercaptobutyramidobenzthiazole, and alkali metal salts of said compounds.

EDWARD B. KNOTT.
PHILIP K. BROOKS.

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