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TONE-CONTROL AGENTS FOR SILVER HALIDE EMULSIONS

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This invention relates to the production of photographic light-sensitive emulsions and to the production of photographic light-sensitive elements including layers of such emulsions.

It is well known that photographic emulsions consisting predominantly of silver chloride, unless steps are taken to prevent it, yield on development images which tend to be greenish-black or brownish-black rather than a good neutral black. This phenomenon also occurs to some extent in the case of emulsions consisting predominantly of silver bromide, especially fine grain emulsions of this type, but whereas it is known that by the addition of certain compounds it is possible to correct the image colour of silver chloride emulsions so that the images obtained are more of a bluish black, the compounds added to such emulsions to produce this correction usually have little or no effect on silver bromide emulsions.

According to the present invention the colour of the developed image in photographic silver halide emulsions, including silver bromide emulsions, is improved by applying to the emulsion, at a stage not later than its development, a small quantity of a compound of the general formula:

$$R_1—CO—NH—NH—C(=S)R_2$$

wherein R_1 is a hydrogen atom or a substituent group, e. g., alkyl (for instance methyl, ethyl, propyl or higher alkyl), aryl (for instance phenyl or naphthyl), aralkyl (for instance benzyl or naphthyl methyl), amino, hydrocarbon-oxy (for instance alkoxy), hydrocarbon thiol (for instance alkyl thiol), alicyclic (for instance cyclopentyl or cyclohexyl) or heterocyclic (for instance furoyl, nicotinoyl, picolinoyl, coumaryl or indolyl) or a substituted group of any of these types, and R_2 is an amino, hydrocarbon-oxy (for instance alkoxy), hydrocarbon thiol (for instance alkyl thiol) or a substituted group of any of these types.

Some typical examples of compounds suitable for use are:

(*a*) Acetyl thiosemicarbazide
$CH_3.CO.NH.NH.CS.NH_2$

(*b*) Formyl-4-ethyl-thiosemicarbazide
$HCO.NH.NH.CS.NH.C_2H_5$

(*c*) Acetyl-dithiocarbazinic acid methyl ester
$CH_3.CO.NH.NH.CS.SCH_3$

(*d*) 1-carbaminyl thiosemicarbazide
$NH_2.CO.NH.NH.CS.NH_2$

(*e*) Benzoyl-dithiocarbazinic acid methyl ester
$C_6H_5.CO.NH.NH.CS.SCH_3$

(*f*) Propionyl-dithiocarbazinic acid methyl ester
$C_2H_5.CO.NH.NH.CS.SCH_3$

(*g*) Carbethoxy-dithiocarbazinic acid methyl ester
$C_2H_5O.CO.NH.NH.CS.SCH_3$

(*h*) Acetyl-dithiocarbazinic acid benzyl ester
$CH_3.CO.NH.NH.CS.SCH_2.C_6H_5$

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(*i*) Acetyl-4:4-diethyl-thiosemicarbazide
$CH_3.CO.NH.NH.CS.N(C_2H_5)_2$

(*j*) Furoyl-dithiocarbazinic acid methyl ester
$(C_4H_3O).CO.NH.NH.CS.SCH_3$

(*k*) Cyclohexyl carbonyl-dithiocarbazinic acid methyl ester
$C_6H_{11}.CO.NH.NH.CS.SCH_3$

(*l*) Butyryl-dithiocarbazinic acid methyl ester
$C_3H_7.CO.NH.NH.CS.SCH_3$

The preparations of compounds (*a*), (*b*), (*d*) and (*e*) are described in Beilstein's "Handbuch der Organische Chemie," 4th edition, compounds (*c*) and (*f*) may be prepared by treating methyl dithiocarbazinate with the appropriate acetic or propionic anhydride or with the appropriate acetyl or propionyl chloride in pyridine, and compound (*g*) may be prepared by treating methyl dithiocarbazinate with ethyl chloroformate in pyridine. Compound (*h*) may be prepared by reacting benzyl dithiocarbazinate with acetic anhydride or acetyl chloride in pyridine and compound (*i*) may be prepared by the analogous method described in Journal für Praktische Chemie, volume 159 at pages 189–192 (1941). Compound (*j*) may be prepared by reacting methyl dithiocarbazinate with furoic anhydride or furoyl chloride, and (*k*) by reacting methyl dithiocarbazinate with cyclohexane carboxylic acid anhydride or chloride. Compound (*l*) may be prepared by reacting methyl dithiocarbazinate with butyric anhydride or butyryl chloride in pyridine. Other compounds included within the scope of this invention may be made by analogous methods using the appropriate starting materials.

The compounds are preferably applied to the emulsions by actual inclusion in the emulsion during its manufacture, or by inclusion in the developing solution with which the photographic element carrying the emulsion is treated. However, they may be included instead in a layer of the photographic element coated adjacent to the emulsion layer, e. g., in a subcoat or supercoat layer, or may be applied to the emulsion from solution prior to development. The invention is of greatest importance in connection with the application of the compounds to fine grain silver iodobromide emulsions.

As indicated above, the compounds should be used in small quantities only. In the case where the compounds are included in the emulsion or in an adjacent layer a proportion of the order of 50 ccs. of a 1% solution of the compound in ethyl alcohol, or other suitable solvent, per litre of emulsion or other coating solution, is generally satisfactory, though the optimum proportion will depend on the nature of the precise compound employed and on the nature of the emulsion or other coating solution in which it is incorporated. Thus a wide range of proportions is practical, e. g., from 1 to 100 ccs. of a 1% solution per litre

of emulsion or other coating solution. When added to the developer solution or applied from solution before development, the compound may conveniently be present in a proportion of the order of 1 part in 5,000–20,000 of such solution. Smaller proportions than these are operative, but usually do not have as large effect as is desired. Higher proportions may be used, but are usually uneconomic. The compounds may be used either as the free compounds or as their metal salts, e. g. their alkali metal salts or silver salts.

All the compounds (*a*) to (*l*) listed above improve the image colour in a silver bromide emulsion or silver iodobromide emulsion when used in any of the ways indicated above, making the resulting developed image a good black which may even tend towards a bluish tint. Compounds (*c*), (*f*) and (*g*) give particularly good results. When the compounds are included in silver chloride emulsions, or added to the developer for such emulsions or otherwise applied to such emulsions at a stage not later than development, they tend to change the image colour from a greenish or brownish black to a bluish-black. The compounds present the further advantage that they do not cause any serious loss in the speed of the emulsions in which they are incorporated.

An approximate measure of the improvement in the tone of the developed emulsion can be obtained by the following method. The silver density of the developed emulsion is measured first through an orange filter which transmits freely from 5900 Å. to the infra-red but absorbs light of lower wavelengths (D_0), and then through a blue filter which transmits light between 3700 Å. and 5100 Å. and absorbs light of other wavelengths (D_B).

The tone index $T=100\times(D_B-D_0)$

A positive figure for T indicates a warm tone and a negative figure a cold tone. In the following table the results obtained with certain of the above compounds are listed, as obtained by adding the compounds to a fine-grain gelatin silver iodobromide emulsion.

Table

Code Letter	Quantity of 1% solution per liter of emulsion	T
	Cc.	
Standard	None	+3
(*a*)	25	−4
(*b*)	5	0
(*c*)	25	−3
(*d*)	25	−1
(*e*)	25	−3
(*f*)	25	−1
(*g*)	25	−2
(*h*)	25	0
(*l*)	25	−2

The above compounds may also be added as their silver salts, for example the compound (*c*) used as its silver salt and added to the same emulsion in equivalent quantity produced an image having a tone index of −1.

What we claim is:

1. A process of improving the colour of the developed image in a photographic silver halide emulsion which comprises applying to the emulsion, at a stage not later than its development, a small quantity of a compound of the general formula:

$$R_1—CO—NH—NH—C(=S)R_2$$

where R_1 is selected from the group consisting of the hydrogen atom and alkyl, aryl, aralkyl, amino, hydrocarbon-oxy, hydrocarbon-thiol, alicyclic and heterocyclic groups, and R_2 is selected from the group consisting of amino, hydrocarbon-oxy and hydrocarbon-thiol groups.

2. A process of improving the colour of the developed image in a photographic fine grain silver iodobromide emulsion which comprises applying to the emulsion, at a stage not later than its development, a small quantity of a compound of the general formula:

$$R_1—CO—NH—NH—C(=S)R_2$$

where R_1 is selected from the group consisting of the hydrogen atom and alkyl, aryl, aralkyl, amino, hydrocarbon-oxy, hydrocarbon-thiol, alicyclic and heterocyclic groups, and R_2 is selected from the group consisting of amino, hydrocarbon-oxy and hydrocarbon-thiol groups.

3. A process of improving the colour of the developed image in a photographic fine grain silver iodobromide emulsion which comprises applying to the emulsion, at a stage not later than its development, a small quantity of a compound of the general formula:

$$R_1—CO—NH—NH—C(=S)R_2$$

where R_1 is a lower alkyl group and R_2 is a lower alkyl thiol group.

4. A process of improving the colour of the developed image in a photographic fine grain silver iodobromide emulsion which comprises including in the emulsion during its manufacture a small quantity of a compound of the general formula:

$$R_1—CO—NH—NH—C(=S)R_2$$

where R_1 is selected from the group consisting of the hydrogen atom and alkyl, aryl, aralkyl, amino, hydrocarbon-oxy, hydrocarbon-thiol, alicyclic and heterocyclic groups, and R_2 is selected from the group consisting of amino, hydrocarbon-oxy and hydrocarbon-thiol groups.

5. A process of improving the colour of the developed image in a photographic fine grain silver iodobromide emulsion which comprises including in the emulsion during its manufacture a small quantity of a compound of the general formula:

$$R_1—CO—NH—NH—C(=S)R_2$$

where R_1 is a lower alkyl group and R_2 is a lower alkyl thiol group.

6. A process of improving the colour of the developed image in a photographic fine grain silver iodobromide emulsion which comprises including in a layer coated adjacent to the emulsion a small quantity of a compound of the general formula:

$$R_1—CO—NH—NH—C(=S)R_2$$

where R_1 is selected from the group consisting of the hydrogen atom and alkyl, aryl, aralkyl, amino, hydrocarbon-oxy, hydrocarbon-thiol, alicyclic and heterocyclic groups, and R_2 is selected from the group consisting of amino, hydrocarbon-oxy and hydrocarbon-thiol groups.

7. A process of improving the colour of the developed image in a photographic fine grain silver iodobromide emulsion which comprises including in a layer coated adjacent to the emulsion a small quantity of a compound of the general formula:

$$R_1—CO—NH—NH—C(=S)R_2$$

where R_1 is a lower alkyl group and R_2 is a lower alkyl thiol group.

8. A process of improving the colour of the developed image in a photographic fine grain silver iodobromide emulsion which comprises developing the emulsion with a photographic developer solution containing a small quantity of a compound of the general formula:

$$R_1—CO—NH—NH—C(=S)R_2$$

where R_1 is selected from the group consisting of the hydrogen atom and alkyl, aryl, aralkyl, amino, hydrocarbon-oxy, hydrocarbon-thiol, alicyclic and heterocyclic groups, and R_2 is selected from the group consisting of amino, hydrocarbon-oxy and hydrocarbon-thiol groups.

9. A process of improving the colour of the developed image in a photographic fine grain silver iodobromide emulsion which comprises developing the emulsion with a photographic developer solution containing a small quantity of a compound of the general formula:

$$R_1—CO—NH—NH—C(=S)R_2$$

where R_1 is a lower alkyl group and R_2 is a lower alkyl thiol group.

10. A process of improving the colour of the developed image in a photographic fine grain silver iodobromide emulsion which comprises including in the emulsion during its manufacture a small quantity of a silver salt of a compound of the general formula:

$$R_1—CO—NH—NH—C(=S)R_2$$

where R_1 is selected from the group consisting of the hydrogen atom and alkyl, aryl, aralkyl, amino, hydrocarbon-oxy, hydrocarbon-thiol, alicyclic and heterocyclic groups, and R_2 is selected from the group consisting of amino, hydrocarbon-oxy and hydrocarbon-thiol groups.

11. A photographic silver halide emulsion containing a small quantity of a compound of the general formula:

$$R_1—CO—NH—NH—C(=S)R_2$$

where R_1 is selected from the group consisting of the hydrogen atom and alkyl, aryl, aralkyl, amino, hydrocarbon-oxy, hydrocarbon-thiol, alicyclic and heterocyclic groups, and R_2 is selected from the group consisting of amino, hydrocarbon-oxy and hydrocarbon-thiol groups.

12. A photographic fine grain silver iodobromide emulsion containing a small quantity of a compound of the general formula:

$$R_1—CO—NH—NH—C(=S)R_2$$

where R_1 is selected from the group consisting of the hydrogen atom and alkyl, aryl, aralkyl, amino, hydrocarbon-oxy, hydrocarbon-thiol, alicyclic and heterocyclic groups, and R_2 is selected from the group consisting of amino, hydrocarbon-oxy and hydrocarbon-thiol groups.

13. A photographic fine grain silver iodobromide emulsion containing a small quantity of a compound of the general formula:

$$R_1—CO—NH—NH—C(=S)R_2$$

where R_1 is a lower alkyl group and R_2 is a lower alkyl thiol group.

14. A photographic element containing a layer of photographic fine grain silver iodobromide emulsion containing a small quantity of a compound of the general formula:

$$R_1—CO—NH—NH—C(=S)R_2$$

where R_1 is selected from the group consisting of the hydrogen atom and alkyl, aryl, aralkyl, amino, hydrocarbon-oxy, hydrocarbon-thiol, alicyclic and heterocyclic groups, and R_2 is selected from the group consisting of amino, hydrocarbon-oxy and hydrocarbon-thiol groups.

15. A photographic element containing a layer of a photographic fine grain silver iodobromide emulsion and, adjacent thereto, a layer containing a small quantity of a compound of the general formula:

$$R_1—CO—NH—NH—C(=S)R_2$$

where R_1 is selected from the group consisting of the hydrogen atom and alkyl, aryl, aralkyl, amino, hydrocarbon-oxy, hydrocarbon-thiol, alicyclic and heterocyclic groups, and R_2 is selected from the group consisting of amino, hydrocarbon-oxy and hydrocarbon-thiol groups.

16. A photographic element containing a layer of a photographic fine grain silver iodobromide emulsion and, adjacent thereto, a layer containing a small quantity of a compound of the general formula:

$$R_1—CO—NH—NH—C(=S)R_2$$

where R_1 is a lower alkyl group and R_2 is a lower alkyl thiol group.

17. A photographic developing solution which includes, in addition to the essential reagents for developing a silver image in a photographic silver halide emulsion, a photographic developing agent and a small quantity of a compound of the general formula:

$$R_1—CO—NH—NH—C(=S)R_2$$

where R_1 is selected from the group consisting of the hydrogen atom and alkyl, aryl, aralkyl, amino, hydrocarbon-oxy, hydrocarbon-thiol, alicyclic and heterocyclic groups, and R_2 is selected from the group consisting of amino, hydrocarbon-oxy and hydrocarbon-thiol groups.

18. A photographic developing solution which includes, in addition to the essential reagents for developing a silver image in a photographic silver halide emulsion, a photographic developing agent and a small quantity of a compound of the general formula:

$$R_1—CO—NH—NH—C(=S)R_2$$

where R_1 is a lower alkyl group and R_2 is a lower alkyl thiol group.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,623,499	Sheppard et al.	Apr. 5, 1927
2,124,159	Weyde	July 19, 1938
2,298,093	Dersch et al.	Oct. 6, 1942
2,346,065	Carroll et al.	Apr. 4, 1944
2,266,442	Schinzel	Dec. 16, 1941
2,276,254	Schinzel	Mar. 10, 1942
2,286,662	Weyde	June 16, 1942
2,309,492	Albers et al.	Jan. 26, 1943
2,311,098	Swan et al.	Feb. 16, 1943

OTHER REFERENCES

Ser. No. 394,290, Bruylants et al., A. P. C. publ. May 4, 1943.