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LIGHT-SENSITIVE SILVER HALIDE EMULSIONS CONTAINING SOLUBLE GOLD SALTS

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U.S. Cl. 96—107

6 Claims

ABSTRACT OF THE DISCLOSURE

Photographic light-sensitive silver halide emulsions comprising as a sensitizer at least one water-soluble gold (I) salt of a mercapto compound comprising a sulphonic acid group in an acid or salt form is described. The sensitizers do not give rise to an increase of the sensitivity to red light when used in combination with sensitizers having a labile sulphur atom as is the case with most gold (I) sensitizers.

The present invention relates to an improved photographic material and more particularly to silver halide emulsion layers having an increased general light-sensitivity and gradation.

In order to increase the light-sensitivity of photographic silver halide emulsions, a whole series of so-called chemical sensitizers is known. Among these chemical sensitizers the so-called sulphur sensitizers i.e. compounds containing a labile sulphur atom e.g. allyl isothiocyanate, thiourea, allyl thiourea, sodium thiosulphate etc. and the gold compounds are particularly worth mentioning. Gold (I) as well as gold (III) compounds have been described for this purpose.

With respect to gelatin, gold (III) compounds act as oxidants with the result that the physical properties of the gelatin are disadvantageously altered. Therefore, gold (I) compounds are favoured.

Gold (I) compounds comprising complex gold (I) ions with a high degree of dissociation such as ammonium dithiocyanato aurate (I), which is commonly used as gold sensitizer, can give rise to complex formation with gelatin i.e. they form little diffusible gold (I)-gelatin complexes whereby sensitization is reduced. In order to remedy this, ripening should take place at elevated temperature and larger amounts of ammonium dithiocyanato aurate (I) should be used; this results, however, in a reduction of the gold salt by the gelatin and in an increase of the fog formation. The formation of gold (I)-gelatin complexes can be reduced considerably by the addition of an excess of thiocyanate ions whereby the dissociation of the dithiocyanato aurate (I) ions is inhibited, but thiocyanate ions are not inert in respect of silver bromide and silver chloride and etch the crystal surface.

It is also possible in the chemical sensitization of light-sensitive silver halide emulsions to combine sulphur sensitization with gold sensitization by simultaneous or subsequent addition to the emulsion of a compound comprising a labile sulphur atom and ammonium dithiocyanato aurate (I). Identical results are obtained by ripening with a gold (I) salt of a compound comprising a labile sulphur atom e.g. dithiurea gold (I) chloride, sodium dithiosulphato aurate (I), etc.

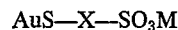
In the combined gold-sulphur sensitization practically no interaction with the gelatin takes place. However, emulsions ripened in this way show a strongly increased sensitivity to red light whereby the possibilities for application of this ripening method are reduced.

It has now been found that gold (I) salts of mercapto

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compounds having a high water-solubility, owing to the presence of a sulphonic acid group in acid or salt form, are very suitable for use as sensitizers for light-sensitive silver halide emulsions.

More particularly, it has been found that gold (I) mercaptides corresponding to the following general formula:



wherein:

X represents a bivalent organic radical e.g. an aliphatic aromatic or heterocyclic bivalent radical such as alkylene including substituted alkylene, arylene including substituted arylene, aralkylene including substituted aralkylene and a bivalent radical comprising a heterocyclic nucleus including a substituted heterocyclic nucleus and

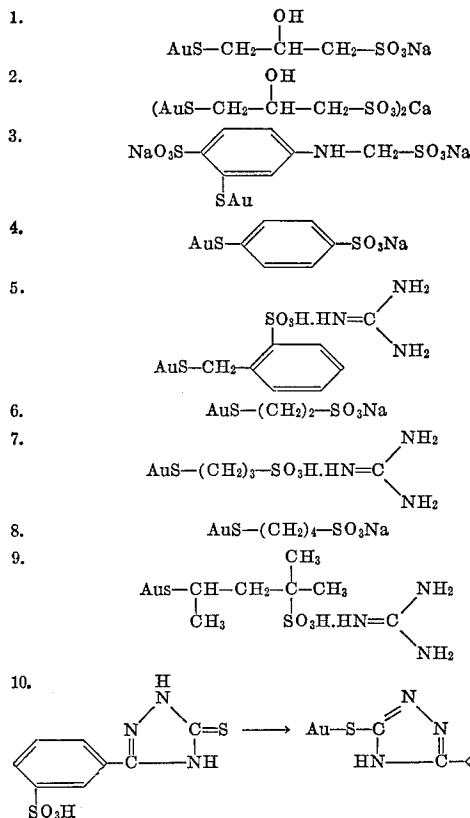
M represents hydrogen, an alkali metal or alkaline earth metal, ammonium, an organic amine, guanidine etc.,

are very suitable for use as gold sensitizers for photographic light-sensitive silver halide emulsions,

The high water-solubility, obtained by the presence of a sulphonic acid group in the gold (I) mercaptide compound, guarantees a homogeneous distribution of the sensitizer in the emulsion. The low degree of dissociation of these gold (I) mercaptides is responsible for the very low interaction with gelatin.

It has further been found that, contrary to the known gold (I) sensitizers, the gold (I) mercaptides of the type described above practically do not give rise to an increase of the sensitivity to red light when used in combination with sensitizers having a labile sulphur atom, particularly when longer ripening times are applied.

Examples of water-soluble gold (I) mercaptides of use according to the present invention are:



The compounds of use according to the present invention can be prepared according to the process described

and claimed in our application filed on even date herewith entitled: "Method for the Preparation of Thiogold (I) Compounds." The following preparations illustrate more particularly how the gold (I) mercaptide compounds can be prepared.

Preparation 1—Compound 7

To a solution of 15.5 g. of 3-mercapto-propane sulphonic acid guanidine salt are added successively: 100 cc. of a concentrated aqueous ammonium hydroxide solution (25% by weight) and 10 g. of hydrogen tetrachloroaurate (III)-4-water dissolved in 50 cc. of water. While stirring and slightly heating the precipitate of gold fulminate formed dissolves gradually. The clear solution is evaporated till dry and the residue is extracted with methanol at the boiling temperature. The gold (I) mercaptide remains as residue. Yield: 90%.

Preparation 2—Compound 10

5 g. of hydrogen tetrachloroaurate (III)-4-water is converted into gold fulminate by means of 75 cc. of a concentrated aqueous ammonium hydroxide solution (25% by weight). The precipitate formed is freed from the excess of ammonium hydroxide by washing with water and decanting. After acidification with hydrochloric acid till pH=1 and addition of 12 g. of 3-(m-sulphophenyl)-1,2,4-triazoline-5-thione the mixture is slightly heated till a clear solution is obtained. Upon cooling the gold (I) mercaptide having Formula 10 above crystallizes. Yield: 8 g. (93%).

The 3-(m-sulphophenyl)-1,2,4-triazoline-5-thione is prepared as follows:

A solution of 121 g. (0.44 mole) of 1-(m-sulphofluorobenzoyl)-thiosemicarbazide in 2 litres of acetone is added to 1.5 litres of N sodium hydroxide. The acetone is removed by evaporation and the residual aqueous solution is refluxed for 4 hours. After cooling the solution is conducted over the cation exchange resin IR 120 and the eluate is evaporated till dry. The resulting product is dried over phosphorus pentoxide. Yield: 90 g. (80%).

The water-soluble gold (I) mercaptides of use according to the present invention can be added to the light-sensitive silver halide emulsion during different preparation steps of the light-sensitive material. They are preferably added to the silver halide emulsion composition after the physical ripening process and after the soluble salts have been removed from the emulsion by washing.

The optimum amount of gold (I) mercaptide added to the silver halide emulsion depends on the very compound, on the nature of the colloid binding agent for the silver halide grains, and on the amount and the kind of the silver halide in the emulsion. This optimum amount can be determined for each particular emulsion in a very simple way of application of the usual tests. In general, however, the gold (I) mercaptides are added to the light-sensitive material in amounts equivalent to from 0.1 mg. to 100 mg. of metallic gold per mole of silver halide.

As already mentioned above, the step of increasing the sensitivity according to the present invention can be combined with chemical sensitization by means of known chemical sulphur sensitizers e.g. sulphur-containing compounds such as allyl isothiocyanate, allylthiourea, or sodium thiosulphate.

The gold (I) mercaptides applied in the present invention can also be used in combination with stabilizers and fog-inhibiting compounds for the silver halide emulsion, for instance with mercury compounds or organic sulphur-containing compounds that form an insoluble silver salt with silver ions, preferably heterocyclic nitrogen-containing thione compounds such as benzothiazoline-2-thione and 1-phenyl-2-tetrazoline-5-thione, the compounds described in the Belgian patent specifications 571,916 and 571,917 both filed Oct. 10, 1958, by Gevaert Photo-Producten N.V. and compounds of the hydroxytriazolo-

pyrimidine type, e.g. 5-methyl-7-hydroxy-s-triazolo[1,5-a]pyrimidine. The combination with sensitizing and stabilizing cadmium salts in the light-sensitive material as well as in the developing bath can also be applied.

Compounds, which sensitize the photographic emulsion by development acceleration, for example polyalkylene oxides such as polyoxyalkylene derivatives as described in U.K. Patents 920,637, 940,051 and 945,340, onium derivatives of amino-N-oxides as described in the U.S. patent application Ser. No. 573,801, organic onium compounds and polyonium compounds, preferably of the ammonium or sulphonium type, e.g. quaternary tetra-alkylammonium salts, alkylpyridinium salts, bis-alkylene-pyridinium salts, alkylquinoline salts, and tri-alkylsulphonium salts can also be used together with the gold (I) mercaptides according to the invention in the developing solution as well as in the light-sensitive material. Other ingredients, such as colour couplers, developing substances, hardening agents, and wetting agents can also be added to the emulsions in the ordinary way.

The gold (I) sensitizers according to the present invention are suitable for the sensitization of all kinds of light-sensitive silver halide emulsions including silver bromide, silver chloride, silver chlorobromide, silver bromiodide and silver chlorobromo-iodide emulsions.

The sensitivity and gradation of fine-grain as well as of coarse-grain silver halide emulsions is increased by the action of the above-mentioned gold (I) mercaptides. These products can be applied for increasing the sensitivity of X-ray emulsions as well as of the most divergent spectrally or non-spectrally sensitized emulsions. They can be incorporated into the photographic emulsion for increasing the sensitivity of negative emulsions as well as of positive emulsions.

Although gelatin is preferably used as hydrophilic colloid for the light-sensitive silver halide emulsion other water-soluble colloidal materials or mixtures of them can be used too such as polyvinyl alcohol, zein, casein, alginic acid, carboxymethylcellulose etc.

The following examples illustrate the invention.

EXAMPLE 1

A silver bromide dispersion is prepared by addition at 25° C., in a period of 5 seconds, of a 0.1 molar solution of silver nitrate to a 0.1 molar solution of potassium bromide. The ratio of volume of both solutions is chosen so that finally a 0.013 molar excess of potassium bromide is present. After 48 hours the liquid is decanted from the precipitate. The precipitate is stirred with water to form a suspension containing 50 g. of silver bromide per liter. The pH of the suspension is comprised between 6.3 and 6.8 and the pAg between 8.4 and 8.7. The suspension is then divided into two aliquot portions A and B. To portion B inert gelatin (the labile sulphur content of the gelatin is less than 1 gamma per gram of gelatin) is added up to a concentration of gelatin of 7.5%.

To each of suspensions A and B is added ammonium dithiocyanato aurate (I) (A₁ and B₁) or the gold (I) salt of 3-mercapto-propane sulphonic acid sodium salt (A₂ and B₂) in the amounts given in Table I below.

The suspensions are then ripened at 30° C. and 55° C. whereupon to the suspensions A an amount of inert gelatin is added up to a concentration of 7.5%. The suspensions are then separately applied to a cellulose triacetate support and dried.

All test strips A₁, B₁, A₂ and B₂ obtained are then image-wise exposed for 1/10 sec. through a wedge with constant 0.15 by means of a 500 watt lamp having a colour temperature of 2,850° K.

The exposed film-strips are then developed at 20° C. for 5 min. in a developing bath having the following composition:

Water—800 cc.
p-Monomethylaminophenol hemisulphate—0.5 g.
Sodium sulphite (cryst.)—100 g.

Hydroquinone—5 g.
Sodium carbonate (cryst.)—80 g.
Potassium bromide—2 g.
Citric acid—2 g.
Water up to—1000 cc.

Of each material, the resulting densities corresponding with a log It. value of 2.40 are measured and listed in the following Table I.

TABLE I

Test strip	Amount of gold (I) sensitizer given in mg. of metallic gold per 50 g. of silver bromide	Density corresponding with log It.=2.40				
		After a ripening time at 30° C. of—		After a ripening time at 55° C. of—		
		1 h.	2 h.	1 h.	2 h.	4 h.
A ₁ -----	0.6	1.15	1.35	1.37	1.43	1.47
B ₁ -----	0.6	0.42	0.50	0.47	0.80	1.05
B ₁ -----	6	0.62	0.73	0.78	1.41	1.38
B ₁ -----	20	0.75	1.01	0.98	1.52	1.57
A ₂ -----	0.6	0.98	1.30	1.31	1.37	1.45
B ₂ -----	0.6	0.91	1.21	1.18	1.40	1.51

From the results in the Table I it clearly appears that the sensitizing activity of the gold (I) mercaptide is only slightly influenced by the presence of gelatin. On the contrary, the ammonium dithiocyanate aurate (I) shows a marked decrease of activity in the presence of gelatin.

EXAMPLE 2

Two silver bromide dispersions A and B are prepared as described in Example 1. Both dispersions are divided into three aliquot portions to which are added respectively per 50 g. of silver bromide: 9 mg. of sodium thiosulphate (Aa and Ba), an amount of sodium di(thiosulphato) aurate (I) equivalent to 6 mg. of gold (Ab and Bb), and an amount of the gold (I) salt of 3-mercaptopropane sulphonic acid guanidine salt equivalent to 6 mg. of gold together with 9 mg. of sodium thiosulphate (Ac and Bc). The 6 mixtures are ripened at 55° C. To the dispersions Aa, Ab and Ac an amount of inert gelatin is then added up to a concentration of 7.5%.

The dispersions are then coated, dried, exposed and developed as described in Example 1.

Of each material, the resulting densities corresponding with a log It. value of 2.40 are measured and listed in the following Table II.

TABLE II

Test strip	Density corresponding with log It.=2.40 after a ripening time of—			
	30 min.	60 min.	90 min.	120 min.
Aa-----	0.45	0.68	0.81	1.35
Ab-----	1.18	1.28	1.32	1.28
Ac-----	1.20	1.23	1.27	1.11
Ba-----	0.40	0.65	0.90	1.45
Bb-----	1.37	1.40	1.45	1.37
Bc-----	1.24	1.30	1.33	1.37

Similar film strips Aa, Ab, Ac, Ba, Bb, Bc are examined as to their sensitivity to red light. For this reason they are exposed with a light-intensity of 67 lux for 3 to 10 min. through an orange "GEVINAC L552" filter (trade name for a darkroom safelight filter from Gevaert-Agfa N.V., Belgium). The strips are then developed in a developing bath as described in Example 1. The densities obtained are listed in the following Table III.

TABLE III

Test strip	Density after a ripening time of—			
	2 hours	3 hours	4 hours	5 hours
Ab-----	0.20	0.28	0.35	0.43
Ac-----	0.11	0.11	0.13	0.14
Ba-----	0.18	0.35	0.50	0.55
Bb-----	0.43	0.52	0.57	0.62
Bc-----	0.14	0.15	0.17	0.17

From the results listed in Tables II and III it appears that in the combined gold-sulphur sensitization practically no interaction with gelatin takes place but that said combination, in the case of known gold (I) sensitizers, gives rise to a marked increase of the sensitivity to red light which is not the case when in the said combination a gold (I) mercaptide according to the invention is used.

EXAMPLE 3

A solution of 100 g. of silver nitrate in 1 litre of water is added at 47° C. in 30 sec. to a solution of 70 g. of potassium bromide, 1 g. of potassium iodide and 25 g. of gelatin in 500 cc. of water. After 10 min. another 80 g. of gelatin are added and the whole is gelled after 30 min. The soluble salts are then removed by washing with water. The emulsion is divided into several aliquot portions and to the separate portions is added one of the gold (I) sensitizers listed in Table IV below.

Thereupon the emulsion portions are chemically ripened at 50° C. for 5 hours. All emulsion portions are then further treated as in Example 1. The sensitometric results obtained are listed in the following Table IV.

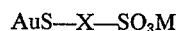
TABLE IV

Gold (I) compound	Fog	Gamma	Density corresponding with log It.=2.40	Dark room sensitivity ¹
An amount of ammonium di (thiocyanato) aurate (I) equivalent to 3 mg. of metallic gold-----	0.03	0.69	1.61	-----
An amount of sodium di (thiosulphato) aurate (I) equivalent to 3 mg. of metallic gold-----	0.06	2.20	3.15	0.28
An amount of the gold (I) salt of 3-mercaptopropane sulphonic acid sodium salt equivalent to 3 mg. of metallic gold-----	0.05	2.50	3.36	-----
An amount of the gold (I) salt of 3-mercaptopropane sulphonic acid sodium salt equivalent to 9 mg. of metallic gold-----	0.06	2.49	3.54	0.03

¹ Fog produced by the dark-room illumination of 67 Lux through a dark-room safelight filter as described in Example 2.

We claim:

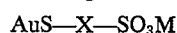
1. Photographic light-sensitive silver halide emulsion containing a sensitizing amount of a gold (I) salt of a mercapto compound which corresponds to the formula:



wherein:

X is a bivalent organic radical, and
M represents hydrogen, an alkali metal, an alkaline earth metal, ammonium, an organic amine or guanidine.

2. Photographic light-sensitive silver halide emulsion according to claim 1, wherein said gold (I) salt of a mercapto compound corresponds to the formula:



wherein:

X is an aliphatic, aromatic or heterocyclic bivalent radical, and

M represents hydrogen, an alkali metal, an alkaline earth metal, ammonium, an organic amine or guanidine.

3. Photographic light-sensitive silver halide emulsion according to claim 1 wherein the gold (I) mercaptide(s) is (are) present in amounts equivalent to from 0.1 to 100 mg. of metallic gold per mole of silver halide.

4. Photographic light-sensitive silver halide emulsion according to claim 1 comprising in addition to the gold (I) mercaptide compound(s) at least one chemical sulphur sensitizer.

5. Photographic light-sensitive material comprising a silver halide emulsion layer formed from a light-sensitive silver halide emulsion according to claim 1.

6. The photographic light sensitive silver halide emul-

sion according to claim 1 wherein the bivalent organic radical is a member of the group consisting of alkylene, arylene, aralkylene and a heterocyclic nucleus.

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U.S. Cl. X.R.

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