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PHOTOGRAPHIC EMULSIONS CONTAINING MERCURY COMPOUNDS AND AZAINDENES

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U.S. Cl. 96—109 9 Claims
Int. Cl. G03c 1/34

The invention relates to photographic silver halide emulsions which are stabilized by means of a combination of special mercury compounds and azaindenes.

Photographic emulsions are mainly characterized by their basic fog level, sensitivity, gradation and granularity. The basic fog level is the slight blackening of an emulsion during development which is due to the fact that some silver halide crystals can be developed without exposure.

It is generally known that the higher the sensitivity of an emulsion, the greater is its basic fog level. In the case of highly sensitive emulsions, the second or chemical ripening process must ripen the emulsion to an increased basic fog level in order to obtain maximum sensitivity and to impart the desired stability to the sensitivity centres on the silver halide crystals of the emulsion.

Since, in general, the basic fog level of photographic emulsions increases during storage, the storage life of highly sensitive emulsions is of course shortened because the fresh fog level is already very high. Such fogging is increased even further by storage under extreme conditions, for example, the high temperatures and high relative air humidity occurring in the tropics. Serious fogging can also be caused by contaminated and carelessly handled developers.

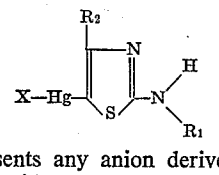
A number of stabilizers and combinations thereof have already been used as fog-inhibiting agents. Examples are heterocyclic mercapto- and amino compounds which form difficultly soluble silver salts, and organic and inorganic mercury compounds.

In view of the progress and the refinements which have been made in methods of preparing silver halide emulsions, particularly with a view to obtaining increased sensitivity, several of the known stabilizers can no longer be used, with the result that there is a great need for more effective methods of stabilizing silver halide emulsions.

It has now been found that a specific combination of stabilizers is surprisingly effective in silver halide emulsions of high and very high sensitivity with regard to any type of actinic light, such as light from the visible wave length range, X-rays or fluorescent light.

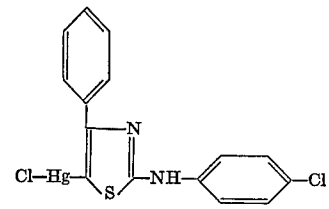
The stabilizer combination according to the invention comprises mercury compounds of aminothiazoles, and azaindene stabilizers.

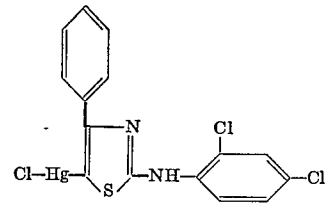
Compounds of the following formula are suitable for use as the aminothiazole mercury compounds:

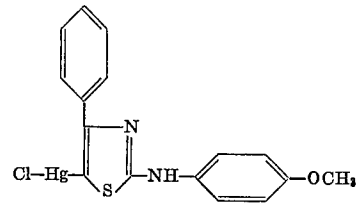


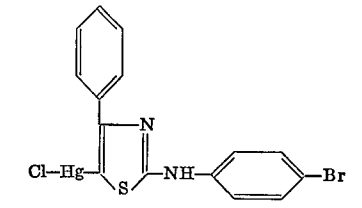
wherein X represents any anion derived from an inorganic or organic acid, such as $CH_3CO.O$—, Cl—, Br—, I—, preferably chloride, and R_1 and R_2 represent phenyl or naphthyl, in particular substituted phenyl or naphthyl, preferred substituents being halogen, such as chlorine or

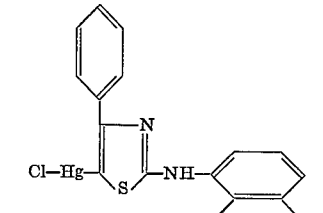
bromine, alkoxy, preferably lower alkoxy having 1 to 5 carbon atoms such as methoxy or ethoxy, and alkyl groups preferably lower alkyl groups having 1 to 5 carbon atoms. In preferred compounds, the substituents are arranged in the ortho- and/or para-position relative to the carbon atom which is bonded to the amino group or to the thiazole ring. The following compounds are mentioned in particular:

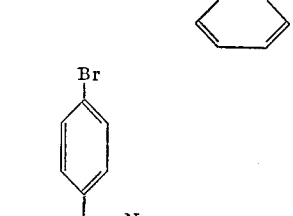












The mercury compounds according to the invention are prepared as described in the article by G. Travagli in Gazz. Chim. Ital., 78, pages 592 to 599 (1948).

In particular, the preparation of Compound 1 is as follows:

14.3 g. of 2-phenylamino-4-phenylthiazole are dissolved at elevated temperature in 150 ml. of glacial acetic acid. 13.6 g. of $HgCl_2$ are then added while stirring. A solution is initially formed but, after a short time, a sub-

stance begins to precipitate in the form of white needles. After boiling for one hour, the product is allowed to cool and is then suction-filtered. Yield: 7.5 g., M.P. 189° C. with decomposition (green-colored).

To purify the compound, it is washed in a little acetone and suction-filtered. It then melts at 199.5° C.

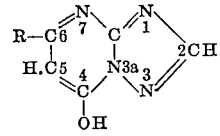
The addition of the compounds set out above to a freshly ripened emulsion considerably reduces the basic fog level. Unfortunately, the emulsion loses one to two degrees of sensitivity, as has occured in the past when mercury compounds were used for stabilization.

If, however, these organic mercury compounds are combined with azaindenes in which at least one N-atom is in the six-membered ring, the sensitivity is surprisingly increased again to the original level of the non-stabilized emulsion without any increase in the fog level.

The effect of the combination of stabilizers according to the invention is particularly surprising because combinations of the mercury compounds used according to the invention with other known stabilizers, such as heterocyclic mercapto compounds, for example 1-phenyl-2-mercapto-tetrazole, do not produce a comparable effect. The loss in sensitivity caused by the mercury compound is not compensated. In addition, the effect of the azaindenes of the present invention is limited to the mercury compounds of the combination according to the invention. When other mercury compounds are used, for example those of the type described in British patent specification No. 742,219, the loss of sensitivity is not compensated by adding an azaindene stabilizer.

Preferred azaindenes are tetra- or penta-azaindenes, in particular those which are substituted by hydroxyl or amino groups. Compounds of this type are described in the article by Birr in the journal "Wissenschaftliche Photographie," vol. 47, (1952), pages 2 to 28, as well as in U.S. Patents 2,444,605, 2,444,606, 2,444,607, 2,450,-397, 2,716,062, 2,735,769, 2,743,180, 2,756,147, 2,835,-581, 2,837,521, 2,852,375, and in German Patent 975,582. (As to the nomenclature and structure of these compounds compare Allen et al. in "Journal of Organic Chemistry" vol. 24 (1959), pages 779 to 802.)

Especially suitable azaindenes may be represented by the following formula:



wherein R stands for an alkyl group, such as methyl, ethyl, propyl.

Specific examples of suitable azaindenes are:

4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene,
4-hydroxy-5-chloro-6-methyl-1,3,3a,7-tetrazaindene,
4-hydroxy-5-carboxy-1,3,3a,7-tetrazaindene,
5-amino-7-hydroxy-1,2,3,4,6-pentazaindene,
5-methyl-7-hydroxy-1,2,3,4,6-pentazaindene,
5,7-diamino-1,2,3,4,6-pentazaindene,
4-hydroxy-6-methyl-1,2,3,3a,7-pentazaindene,
4-hydroxy-6-methyl-1,3a,7-triazaindene.
2-methyl-4-hydroxy-6-methyl-3,3a,7-triazaindene,
4-hydroxy-6-ethyl-1,3,3a,7-tetrazaindene,
2-methyl-4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene,
2-hydroxymethyl-4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene,
4-amino-6-methyl-1,3,3a,7-tetrazaindene,
4-amino-5-ethyl-6-methyl-1,3,3a,7-tetrazaindene.

The combination according to the invention not only improves the fresh fog level of the emulsion, it also reduces the increase in fogging during storage. This can be proved by a short-time test in which the cast film samples are stored for 3 days at 60° C. and compared with a standard sample stored under normal conditions.

The combination of stabilizers according to the invention may be used in a variety of silver halide emulsions. Highly sensitive silver bromide emulsions which may also contain silver iodide, preferably up to 10 mol percent, are preferred. Gelatin is preferably used as the binder for the emulsion, although it may be partly or completely replaced by other hydrophilic and water-permeable binders. Such materials include, for example, polyvinyl alcohol, polyvinyl pyrrolidone, alginic acid or its derivatives, and carboxymethyl cellulose. The emulsions may be optically sensitized with the conventional cyanine and merocyanine dyes.

The emulsions may be chemically sensitized by any one of the known processes, for example with sulfur compounds or noble metal salts, for example of gold, palladium, platinum, iridium, ruthenium or rhodium. They may also be chemically sensitized with reducing agents such as stannous salts or organic polyamides. The combination of stabilizers according to the invention may, in particular, also be used in emulsions chemically sensitized by polyethylene oxide compounds.

Suitable alkylene oxide polymers are derived from alkylene oxides which contain 2 to 4 carbon atoms, that is to say from ethylene oxide, propylene oxide, butylene oxide. The use of the polymers of these alkylene oxides, which are also known as polyalkylene glycols, is described in U.S. Patents 2,423,549 and 2,441,389. Furthermore, there may be employed as chemical sensitizers for the silver halide emulsion layers of the present invention derivatives of polyalkylene oxides which are obtained by condensing an alkylene oxide polymer with an organic compound having an active hydrogen atom or by condensing said latter compound with alkylene oxide during the polymerization thereof.

Suitable organic compounds with active hydrogen atoms are for instance alcohols, primary or secondary amines, acids, amides, phenols, such as monohydric saturated or unsaturated alcohols having 1 to 20 carbon atoms, e.g., ethanol, dodecanol, stearyl alcohol, oleyl alcohol, polyhydric alcohols, e.g., glycols, glycerol, pentaerythritol, trimethylol propane, aliphatic primary or secondary amines, e.g., N-methyl-N-dodecylamine, aliphatic carboxylic acids, e.g., lauric acid, stearic acid, oleic acid or the amides of these acids, furthermore phenol, alkyl phenols, e.g., p-dodecyl phenol. Preferred derivatives of polyalkylene oxides are reaction products of alkylene oxide or of their polymers with compounds containing hydrocarbon radicals with 10 to 20 carbon atoms. The quantity used will depend upon the silver halide content of the emulsion to which the compounds are added. It can vary from 0.01 g. to 1 g. per 1 kg. of silver halide emulsion. The preferred quantity being 0.05 to 2 g. per 1 mol of silver halide. The optimum quantity can easily be established empirically for each emulsion.

Suitable chemical sensitizers of the above type may be illustrated by the following formula:

$$R.O(CH_2.CH_2.O)_nH$$

wherein R stands for hydrogen, an alkyl radical (e.g., ethyl, dodecyl, oleyl), an acyl radical of an organic carboxylic acid (e.g., lauric acid, oleic acid), a phenyl radical (e.g., phenyl, p-dodecylphenyl) and n=an integer greater than about 30. Also suitable as chemical sensitizers containing polyalkylenes oxide groups are the condensation products of spirocyclic pentaerythritol - di - (phosphoric acid monohalides) and polyethylene glycols consisting of between 3 and 100 ethylene glycol units, as they are disclosed in U.S. Patent 3,169,863 and U.S. patent application Ser. No. 368,714.

The emulsions may be hardened in the usual way, for example with formaldehyde, halogen-substituted aldehydes containing a carboxyl group, such as mucobromic acid, diketones, methane sulfonic acid esters or dialdehydes.

The stabilizers are added to the emulsions, for example, in the following concentrations: (1) mercury compound: 0.2 to 100 mg. per mol of silver halide; (2) azaindene; 10 mg. to 10 g. per mol of silver halide.

Example 1

A standard, highly sensitive silver iodobromide gelatin emulsion (2 mol percent of silver iodide) which contains 80 g. of silver halide per liter, is sensitized with gold salts, and in addition—contains the usual wetting agents, for example—saponin, and hardening agents such as formaldehyde, is divided up into three parts. Each part or sample is mixed with the quantity indicated in Table I of one of a variety of stabilizers, and is then cast as usual onto a transparent substrate and dried.

Each sample is then exposed behind a step wedge and developed for about 5 minutes at 20° C. in the following developer mixture: 3.5 g. of p-methylaminophenol sulfate, 60 g. of anhydrous sodium sulfite, 9 g. of hydroquinone, 40 g. of anhydrous soda and 3.5 g. of potassium bromide, dissolved in about 750 ml. of water and made up with water to 1 liter. The relative sensitivity, the gamma value and the fog level are determined in the usual way. The results are given in Table I.

TABLE I

Sample stabilizer	Quantity per liter of emulsion, mg.	Sensitivity difference in degrees DIN	Fog level	γ
A—— Azaindene	200	Control	0.17	2.6
B—— Compound 2	0.8	−3	0.14	2.5
C—— Azaindene plus Compound 2——	200+0.8	0	0.14	2.8

The results show that the mercury compound reduces fogging very considerably, but at the same time reduces sensitivity. By using the combination with the azaindene, the low fog level is maintained and the original sensitivity recovered. 5-methyl-7-hydroxy triazaindolizine was used as the azaindene.

Example 2

A standard, highly sensitive silver iodobromide gelatin emulsion (2 mol percent of silver iodide) which contains 80 g. of silver halide, is sensitized with gold salts, and in addition contains the usual wetting agents such as saponin, and hardening agents such as formaldehyde, is divided up into three parts. Each part is then mixed with the quantity indicated in Table II of one of a variety of stabilizers, and is then cast in the usual way onto a transparent substrate and dried.

Each sample is exposed behind a grey wedge and developed for about 5 minutes at 20° C. in the developer mixture described in Example 1.

The relative sensitivity, the gamma value and the fog level are determined in the usual way. The results are given in Table II.

TABLE II

Sample stabilizer	Quantity per liter of emulsion, mg.	Sensitivity difference in degrees DIN	Fog level	γ
A—— Azaindene	200	Control	0.14	1.7
B—— Compound 1	0.8	−2	0.11	1.9
C—— Azaindene plus Compound 1——	200+0.8	0	0.11	1.7

These results show that the mercury compound very considerably reduces fogging, but at the same time also reduces sensitivity. By using the combination with the azaindene, the low fog level is maintained and the original sensitivity level recovered. 5-methyl-7-hydroxy-triazaindolizine was used as the azaindene.

Example 3

The effectiveness of a combination of stabilizers according to the invention is tested as described in the preceding two examples. The results are given in Table III:

TABLE III

Sample stabilizer	Quantity per liter of emulsion, mg.	Sensitivity difference in degrees DIN	Fog level	γ
A—— Azaindene	200	Control	0.12	1.8
B—— Compound 3	0.2	−1.5	0.10	1.6
C—— Azaindene plus Compound 3——	200+0.2	0	0.10	1.6

Example 4

Following the procedure described in Example 1, various samples are prepared which are additionally coated with a protective layer consisting of gelatin containing 160 mg. of a chemical sensitizer which is a condensation product of spirocyclic pentaerythritol-di-(phosphoric acid monochloride) and polyethylene glycol containing 20 ethylene oxide units according to French Patents 1,364,351 or 1,396,860.

The materials are tested in the same way as in Example 1. The results of the tests are shown in Table IVA. The behaviour of the photographic materials after 3 days' storage in a heating chamber at 60° C., is apparent from Table IVB.

TABLE IVA

Sample stabilizer	Quantity per liter of emulsion, mg.	Relative sensitivity difference in degrees DIN	Fog level	γ
A—— Azaindene	200	+1	0.13	3.4
B—— Azaindene plus Compound 1——	200+0.1	+5	0.10	3.4

TABLE IVB

Sample	Relative sensitivity	Fog level	γ
A	0	0.19	2.9
B	0	0.12	2.8

Example 5

A highly sensitive silver iodobromide gelatin emulsion (6 mol percent of silver iodide) which contains 60 g. of silver halide per kg. of emulsion and which is panchromatically sensitized in the usual way, is divided up into 4 samples. Various additives are introduced into the four samples each of which is then further processed as described in Example 1 in a p-methylaminophenol-hydroquinone-borax developer. The results of the com-

parative tests are given in Table V which relates to a test carried out on the four samples after they had been stored for 3 days at 60° C. in a heating chamber.

TABLE V

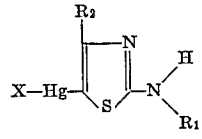
Sample stabilizer	Quantity per liter emulsion, mg.	Polyethylene oxide	Relative sensitivity in degrees DIN	Fog level	γ
A------ Azaindene	200	P80----------	−2----------	0.18	0.50
B------ Azaindene plus Compound 1---	200+0.4	P80----------	0----------	0.13	0.55
C------ Azaindene	200	P90----------	−1.5° C---------	0.15	0.50
D------ Azaindene plus Compound 1---	200+0.4	P90----------	0----------	0.12	0.50

The polyethylene oxide P80 is a polyaddition product of about 80 mols of ethylene oxide and 1 mol of oleyl alcohol. The material is added to the emulsion in quantities of 160 mg. per liter.

The polyethylene oxide P90 is a product of the type described in Belgian patent specification 635,167 which contains about 90 polyethylene oxide units. It is added to the emulsion in quantities of 320 mg. per liter.

What we claim is:

1. A photosensitive photographic material comprising a silver halide emulsion layer which is stabilized by an azaindene and an aminothiazole mercury compound corresponding to the following formula:

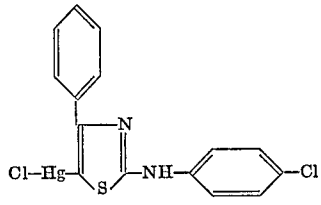


wherein X represents an anion and R_1 and R_2 each represent a phenyl or naphthyl grouping.

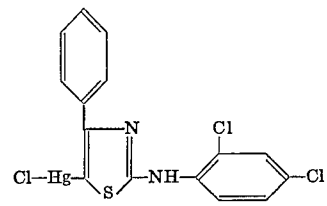
2. A photosensitive photographic material as claimed in claim 1, wherein R_1, R_2 or R_1 and R_2 represent phenyl substituted in the ortho, para, or ortho and para-position by a halogen atom or an alkoxy group.

3. A photosensitive photographic material as claimed in claim 1, wherein the photosensitive silver halide emulsion layer contains the azaindene in quantities of 10 mg. to 10 g. per mol of silver halide and the mercury compound in quantities of 0.2 to 100 mg. per mol of silver halide.

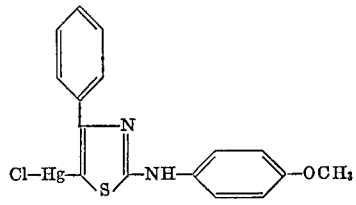
4. A photosensitive photographic material as claimed in claim 1, wherein the aminothiazole mercury compound is a compound of the formula



5. A photosensitive photographic material as claimed in claim 1, wherein the aminothiazole mercury compound is a compound of the following formula



6. A photosensitive photographic material as claimed in claim 1, wherein the aminothiazole mercury compound is a compound of the formula



7. A photosensitive photographic material as claimed in claim 1, wherein the photosensitive silver halide emulsion layer contains in addition to said azaindene and said aminothiazol mercury compound, a sensitizing amount of a chemical sensitizer containing polyethylene oxide groups.

8. A photosensitive photographic material as claimed in claim 1 wherein the azaindene is a tetra- or penta-azaindene substituted by hydroxyl or amino groups.

9. A photosensitive photographic material as claimed in claim 2 wherein the halogen atom is chlorine or bromine and the alkoxy group has not over 5 carbon atoms.

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