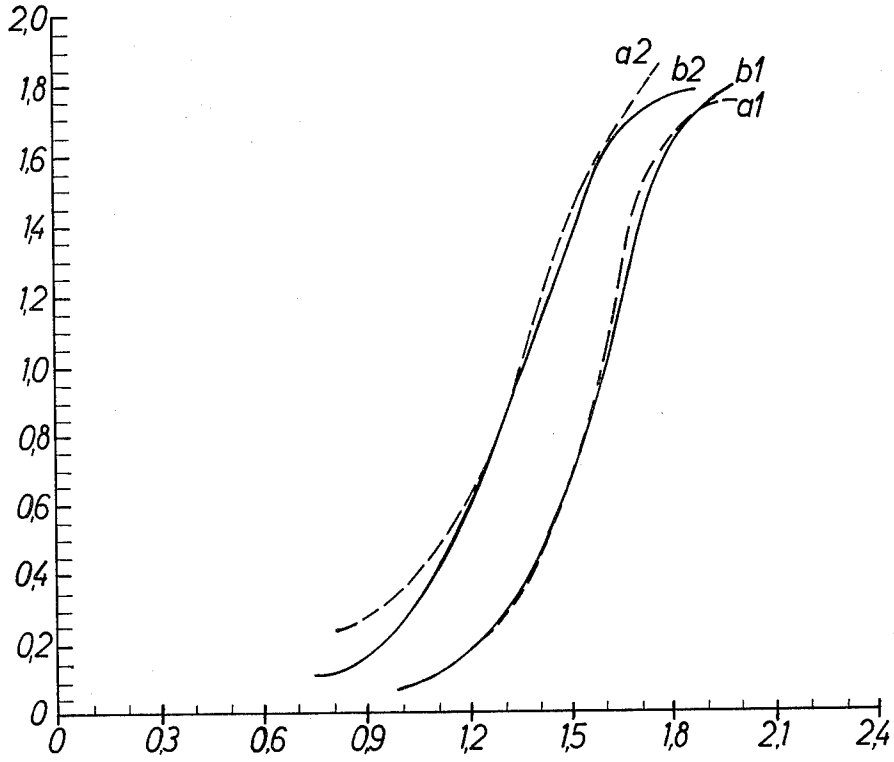
May 24, 1966 J. GÖTZE ETAL 3,252,799

STABILIZED SILVER HALIDE EMULSIONS

Filed May 7, 1963 2 Sheets-Sheet 1

FIG. 1



INVENTORS:
JOHANNES GÖTZE, GÜNTHER KOEPKE.
BY
Connolly and Hutz
their ATTORNEYS

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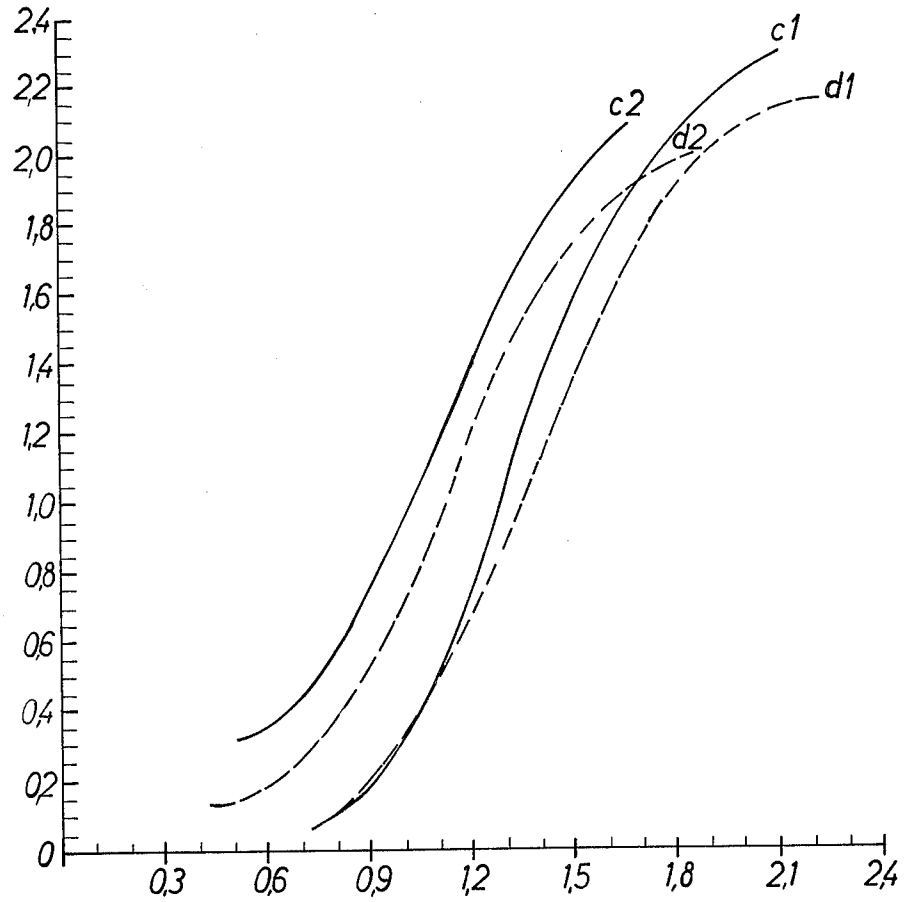
FIG. 2



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STABILIZED SILVER HALIDE EMULSIONS

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8 Claims. (Cl. 96—109)

The present invention relates to novel stabilizers for silver halide emulsions as well as to stabilized photographic materials containing the said stabilizers.

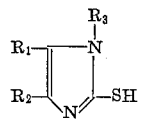
Photographic materials containing silver halide gelatine emulsion layers generally change their properties when stored. They may, for example, show an increased tendency to fog. This may be due to storage alone or may be due to mechanical stress. Fogging produced through mechanical stress is called mechanical fogging.

The sensitivity of the emulsion may also change and may either increase or decrease. The gradation often changes as well, usually becoming flatter.

It is customary to add stabilizing compounds to the emulsions to prevent these changes. These compounds must be very carefully selected because they must not impair the photographic properties of the emulsion. For this reason, the number of stabilizers that can be used in practice is small. Most of the stabilizing compounds that have been described cannot be used because they reduce the sensitivity of an emulsion to a greater or less extent. The most important stabilizers are those from the triazaindolizine series, which have been known for decades.

Since, however, as described above, these products must stabilize a number of different properties of the emulsion, it is generally necessary to use a combination of different stabilizers so that care must be taken to choose stabilizers which are compatible with one another.

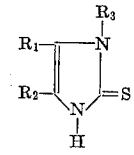
It has been found that the properties of the silver halide emulsion may be considerably improved by adding mercaptoimidazoles of the general formula



(I)

In this formula, R_1 and R_2 represent aryl radicals such as phenyl or naphthyl or heterocyclic radicals such as furyl, thienyl or pyridyl. R_3 represents an alkyl radical preferably lower alkyl or, like R_1 and R_2, an aryl such as phenyl or naphthyl or heterocyclic radical. The choice of radicals, particularly of the heterocyclic radicals, will be dictated mainly from the point of view of the process of preparation. The substituents R_1, R_2 and R_3 may themselves be further substituted. The type of these substituents are not critical. The advantageous effect of the imidazole derivatives according to the invention is based on the mercaptoimidazole structure of the general formula given above. Preferred are compounds in which R_1 and R_2 are phenyl, furyl or thienyl and R_3 are aryl or heterocyclic radicals or generally compounds having a relatively high molecular weight, for instance those in which the substituents R_1, R_2 and R_3 are aryl radicals such as phenyl or naphthyl.

The mercaptoimidazoles of the general Formula I may be in equilibrium with the tautomeric thione which is represented by the following general Formula II:

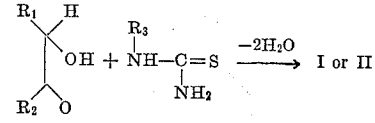


(II)

With regard to the use of the compounds according to the invention it is, of course, immaterial which of the tautomers represents the active form.

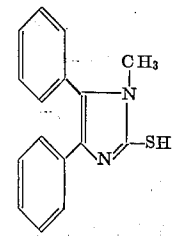
The particular advantage of the stabilizers according to the invention lies in their wide range of effectiveness. These compounds stabilize practically all the properties of an emulsion mentioned earlier. Thus, for example, the imidazoles according to the invention eliminate the sensitivity of photographic silver bromide emulsions to mechanical stress and considerably increase the stability to storing. In the case of color emulsions, for example, this has the effect that the white tones are preserved after prolonged storage and that the flattening of the gradation is prevented.

The mercaptoimidazoles are according to the invention insoluble or only sparingly soluble in water and alcohols etc. and do not dissolve in dilute aqueous alkalies. To prepare the imidazoles, acyloins (III) e.g., benzoin, furoin, p,p'-dichlorobenzoin, p,p'-dimethoxybenzoin, piperoin, benzfuroin and other acyloins are boiled for several hours with N-alkyl- or N-aryl thioureas (IV) in hexanol or other suitable solvents. The water produced in the reaction is distilled off during the reaction. The desired imidazoles are either precipitated during the reaction or crystallize on cooling.



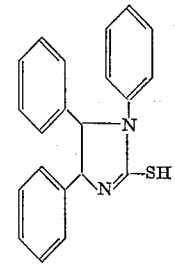
The products are purified by recrystallizing from glacial acetic acid or from a mixture of dimethylformamide and alcohol. The melting points lie in the region of 300° C. or more. The following are examples of imidazoles according to the invention:

(1)



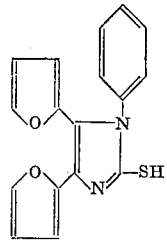
1-methyl-2-mercapto-4 :5-diphenylimidazole

(2)



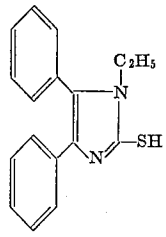
1 :4 :5-triphenyl-2-mercaptoimidazole

(3)



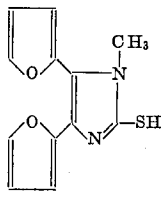
1-phenyl-2-mercapto-4 :5-difurylimidazole

(4)



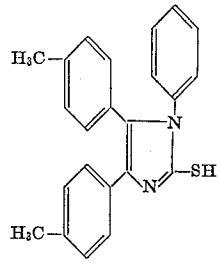
1-ethyl-2-mercapto-4 :5-diphenylimidazole

(5)



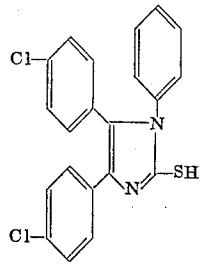
1-methyl-2-mercapto-4 :5-difurylimidazole

(6)



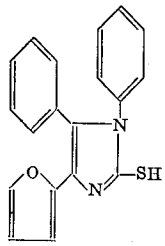
1-phenyl-2-mercapto-4 :5-di(p-methylphenyl)-imidazole

(7)



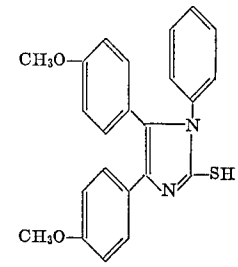
1-phenyl-2-mercapto-4 :5-di-(p-chlorophenyl)-imidazole

(8)



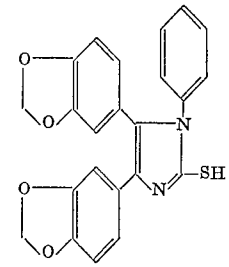
1 :5-diphenyl-2-mercapto-4-furyl-imidazole

(9)



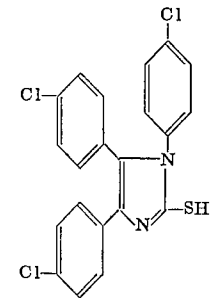
1-phenyl-2-mercapto-4 :5-di-(p-methoxyphenyl)-imidazole

(10)



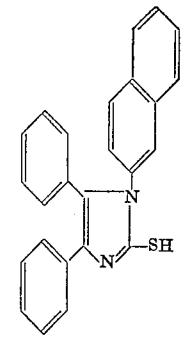
1-phenyl-2-mercapto-4 :5-di-(methylenedioxyphenyl)-imidazole

(11)



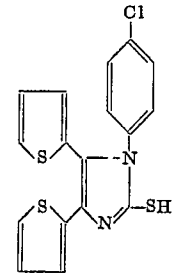
1 :4.5-tri-(p-chlorophenyl)-2-mercapto-imidazole

(12)



1-β-naphthyl-2-mercapto-4 :5-diphenylimidazole

(13)



1-(p-chlorophenyl)-2-mercapto-4 :5-di-thienyl-imidazole

The substances are added in quantities of 0.25 to 1 millimol per 0.15 mol Ag to the emulsion before the emulsion is poured. The emulsion may be prepared with a silver-gelatine ratio of 1:4 to 1:1.5.

The following examples are given to illustrate the application and mode of action of the imidazole derivatives according to the invention:

Example 1

The usual additives such as hardeners, e.g., formalin or chrome alum or wetting agents such as saponine are added to an unwatered silver chlorobromide type of silver halide emulsion which may be sensitized. In addition, 396 mg. (=1 mmol) of the compound according to Formula 7, dissolved in dimethylformamide are added per kg. of emulsion (corresponding to 0.17 mol Ag). The whites of a layer of this emulsion are better than the whites of a layer of the same emulsion without imidazole additive. Then this emulsion layer and a standard emulsion layer without additive are stored at 60° C. and 40% relative humidity for 3 days, the gradation of the unstabilized emulsion is flattened by two steps of a test wedge, whereas that of the stabilized emulsion is flattened by hardly one step. The unstabilized emulsion is fogged whereas the stabilized emulsion is free from fog. The effect of the substance is illustrated in FIGURE 1.

Curves a_1 and a_2 relate to the emulsion without stabilizer additive. a_1 gives the gradation of a fresh emulsion and a_2 gives that of an emulsion treated in a heating cupboard. Curves b_1 and b_2 relate to the above emulsion containing compound 7. The emulsion corresponding to curves b_1 and b_2 were treated in the same way as described for the emulsion corresponding to curves a_1 and a_2.

Example 2

The usual hardening and wetting agents as well as a color component of the β-dicarbonylamide type which gives a yellow dyestuff after chromogenic development are added to a silver halide emulsion. A suitable component is described in Bios Report No. 1605, page 25 (Ta 521). In addition, 356 mg. of compound 6, dissolved in dimethylformamide are added to 1 kg. of emulsion. The whites of such a layer are better than the whites of a layer made from the same emulsion but containing, instead of the stabilizer according to the invention, 400 mg. (=2.67 mmol) of a stabilizer of the triazaindolizine type, e.g., 5-methyl-7-hydroxy-1:3:4-triazaindolizine. Artificial ageing under the conditions described in Example 1 does not alter the gradation of the emulsion stabilized according to the invention whereas the gradation of the layer stabilized with triazaindolizine increases by one step. In addition, the emulsion remains free from fog. The results of the comparison test are shown in FIGURE 2 where curves c_1 and c_2 relate to the stabilizer used for comparison and curves d_1 and d_2 relate to the emulsion containing compound 6. The two curves have the same meaning as described in Example 1.

Example 3

The dependence of the stabilizing effect on the quantity of imidazole compound added is demonstrated by the following experiment. An emulsion according to Example 2 is treated with decreasing quantities of the substance according to Formula 7. The results of artificial ageing (see Example 1) are shown in the following table:

Mmol of substance according to Formula 7 per 1 kg. emulsion	Change in gradation on ageing	Fogging on ageing (color fogging measured against a standard with blue filter)
1.0	----------	0.03
0.5	+0.4	0.08
0.25	+0.6	0.12
0.1	+1.3	0.18
0	+2.0	0.24

Example 4

An emulsion as described in Example 2 is treated with hardening agents, wetting agents and a color component (see Example 2) and with 187 mg. of a substance according to Formula 12, dissolved in dimethylformamide, per 1 kg. emulsion. On artificial aging, the gradation changes by 0.6 step, the gradation of the emulsion used for comparison changes by two steps and at the same time there is strong fogging of the comparison emulsion (comparison of color fogging 0.03 against 0.24).

Example 5

An emulsion as described in Example 2 is treated with hardening and wetting agents and with a color component (see Example 2) and with 77 mg. (0.25 mmol) of a substance according to Formula 3, per 1 kg. of emulsion. In the heating cupboard, the gradation of a layer of this emulsion changes by 0.5 of a step whereas in an emulsion containing the comparison stabilizer, the gradation changes by two steps and at the same time there is strong fogging.

Example 6

An emulsion as described in Example 2 treated with hardening agents, wetting agents and a color component (see Example 2) is also treated with 430 mg. (1 mmol) of an imidazole according to Formula 11, dissolved in dimethyl formamide, per 1 kg. of emulsion and the emulsion is then cast. After applying an intermediate layer, a green sensitive silver chloride emulsion which contains a color component for producing a magenta image, e.g., 1 - (4' - phenoxy-3'-sulpho-phenyl)-3-heptadecyl-pyrazolone-(5), is cast on to this layer, and after applying another intermediate layer, a red sensitive silver chloride emulsion which contains a color component for producing a cyan image, e.g. 2-hexadecyl-carbonamido-4-sulphonaphthol-(1) is cast thereon. The three layer material thereby produced has better whites than a material built up similarly but with the comparison stabilizer described in Example 2 instead of the compound 11 according to the invention. When stored in the heating cupboard as described in Example 1, the gradation changes by 0.3 of a step and the layer has no fogging. In the comparison test, the gradation changes by 0.9 of a step and the layer is fogged.

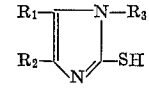
Example 7

328 mg. of an imidazole according to Formula 2 are added to an emulsion described in Example 2 which contains wetting and hardening agents and color components (see Example 2). The whites of a layer of this emulsion are better than those obtained in the comparison test described above. On artificial ageing, the gradation of a stabilized emulsion does not change whereas in the comparison test the gradation increases by 1.8 steps and there is strong fogging.

The stabilizers according to the invention may also be used in silver halide emulsion layers in which the binding agent usually used, namely photographic gelatine, is totally or partially replaced by gelatine substitutes such as polyvinyl pyrrolidone, polyvinyl alcohol, alginic acid derivatives or carboxymethyl cellulose or similar materials. The silver halides may consist of chlorides, bromides, iodides or mixtures thereof.

We claim:

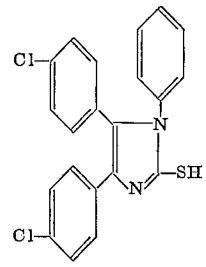
1. A light-sensitive silver halide emulsion containing a stabilizing amount of a compound of the following general formula:



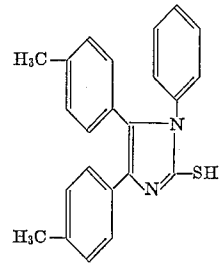
wherein R_1 and R_2 represents a radical selected from the class consisting of aryl and heterocyclic groups and R_3 stands for a member selected from the class consisting of lower alkyl, aryl and a heterocyclic radical.

2. Light-sensitive material according to claim **1**, wherein R_1, R_2 and R_3 are radicals selected from the class consisting of phenyl and naphthyl.

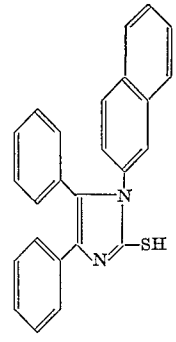
3. Light-sensitive material according to claim **1**, in which the stabilizer compound has the formula:



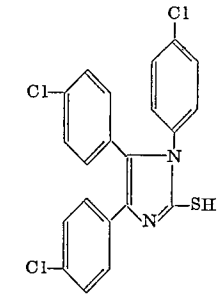
4. Light-sensitive material according to claim **1**, in which the stabilizer compound has the formula:



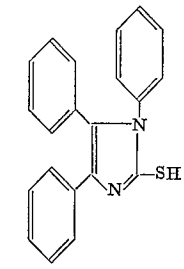
5. Light-sensitive material according to claim **1**, in which the stabilizer compound has the formula:



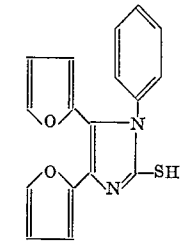
6. Light-sensitive material according to claim **1**, in which the stabilizer compound has the formula:



7. Light-sensitive material according to claim **1**, in which the stabilizer compound has the formula:



8. Light-sensitive photographic material according to claim **1**, in which the stabilizer compound has the formula:



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