United States Patent [19]

Pollet et al.

[11] **3,728,126**

[45] **Apr. 17, 1973**

[54] **SILVER HALIDE EMULSION CONTAINING AN ORGANIC SELENIUM COMPOUND ANTIFOGGING AGENT**

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[22] Filed: **Mar. 6, 1970**

[21] Appl. No.: **17,304**

[30] **Foreign Application Priority Data**

July 3, 1969 Great Britain.....12,234/69

[52] **U.S. Cl.** **96/109,** 96/107, 96/108, 96/52, 96/94

[51] **Int. Cl.** **G03c 1/34**

[58] **Field of Search**.....96/109, 107, 110

[56] **References Cited**

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Attorney—Brufsky, Staas, Breiner and Halsey

[57] **ABSTRACT**

Light-sensitive materials comprising a silver halide emulsion layer and a compound having the formula:

$$R_1—Q—Se—R_2$$

wherein:

Q stands for selenium or sulphur, and

each of R_1 and R_2 (the same or different) stands for an alkyl group, an aralkyl group or an aryl group.

The compound of the general formula inhibits fogging and/or bronzing and/or stabilizes the emulsion.

10 Claims, No Drawings

SILVER HALIDE EMULSION CONTAINING AN ORGANIC SELENIUM COMPOUND ANTIFOGGING AGENT

This invention relates to fog-inhibiting agents, stabilizers and antibronzing agents for photographic light-sensitive silver halide emulsions, and to the use of these compounds in light-sensitive photographic material.

It is well known that light-sensitive silver halide materials comprising gelatin silver halide emulsion layers are subject to fogging. Fogging in general and chemical fogging in particular may be defined as the formation of a uniform deposit of silver on development which is dependent on a whole series of circumstances and factors namely on the nature of the emulsions, on their age, on the conditions under which they have been stored, on the development conditions, etc. For particular development conditions the fog tends to be greater as the time of storage and the temperature and relative humidity of the atmosphere in which the emulsions are stored are increased.

It is also known that the silver image formed after exposure undergoes a degradation, by which is meant a shift and a decrease of intensity of the image-tone during the finishing to a visible image e.g. under the influence of ingredients used in the developing bath, the fixing bath, the coloring bath, and so on. This degradation mainly appears on drying the developed images, whereby a decrease of density and of gradation takes

place and an undesired color or metallic gloss of the developed silver, the so-called "plumming", appears. This phenomenon is particularly pronounced when the photographic images are submitted to hot-glazing or mechanical drying at elevated temperature.

Several compounds have been proposed for use as stabilizers, antifoggants and antibronzing agents. The greater part of these compounds, however, usually exert a strong desensitizing effect on the emulsion.

It has now been found that compounds corresponding to the following general formula :

$$R_1—Q—Se—R_2$$

wherein :

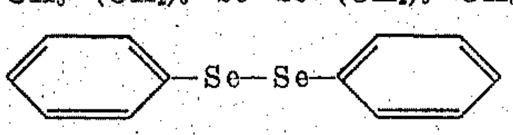
Q stands for selenium or sulphur, and

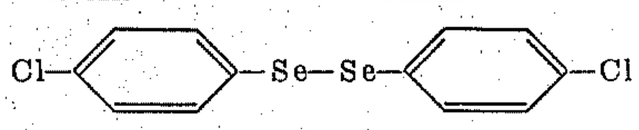
each of R_1 and R_2 (the same or different) stands for an alkyl group, an aralkyl or an aryl group including these groups carrying further substituents such as halogen e.g. chlorine and bromine, carboxyl, nitro, etc.

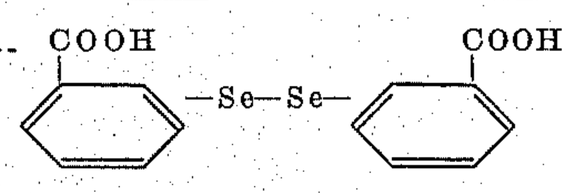
are effective antibronzing agents and exert a fog-inhibiting action on light-sensitive photographic emulsions without giving rise to an appreciable desensitization thereof.

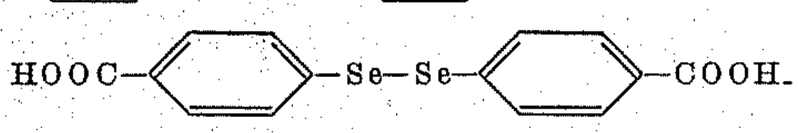
The compounds having the structures listed below are representatives of those falling within the scope of the above general formula. They can be prepared as described in the literature referred to.

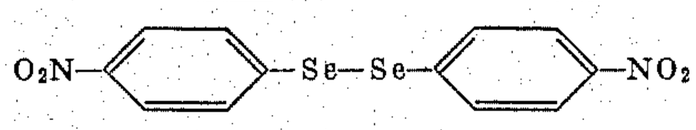
1. $CH_3—(CH_2)_6—Se—Se—(CH_2)_6—CH_3$ — J. Am. Chem. Soc. 82, 2762 (1960).

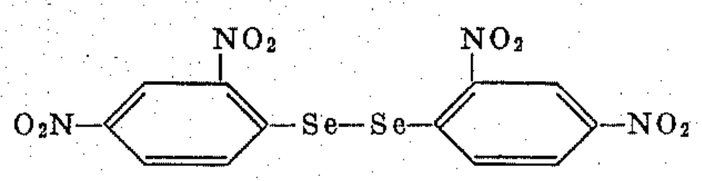
2.  — Ber., 65, 812 (1932).

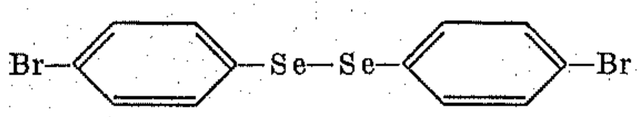
3.  — J. Chem. Soc., 1364 (1926).

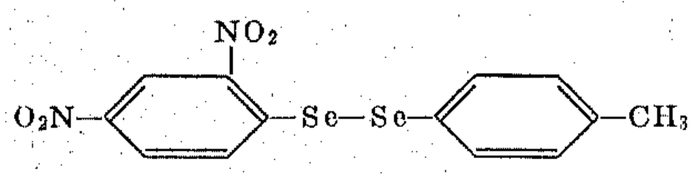
4.  — J. Chem. Soc., 2831 (1952).

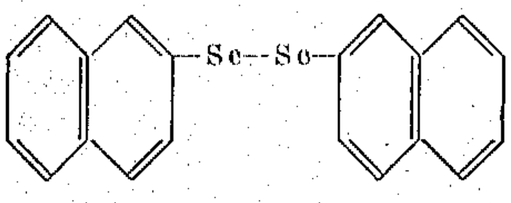
5.  — J. Chem. Soc., 2280 (1928).

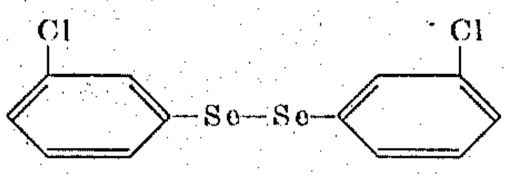
6.  — Houben-Weyl "Methoden der Organischen Chemie" Band XI, 1955, p. 1095.

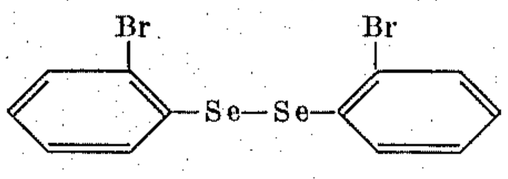
7.  — Ber., 88, 676 (1955).

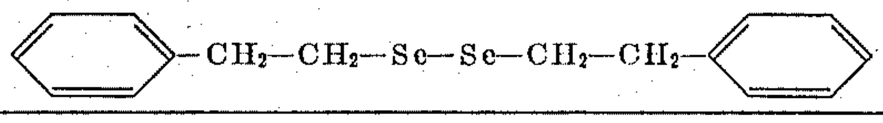
8.  — J. Chem. Soc., 1364 (1926).

9.  — Bull. Soc. Chim., 245 (1950).

10.  — Ber., 92, 40 (1959).

11. 

12.  — J. Org. Chem. 33, 230 (1968).

13. 

Compound 11 was prepared from the Grignard reagent of m-chloro-bromobenzene in anhydrous ether treated with an equimolecular amount of selenium by refluxing for 2 hours with stirring. The mixture was acidified with diluted hydrochloric acid whereupon the ether layer was separated, dried over sodium sulphate and filtered. An air current was conducted through the solution and the latter was distilled.

Compound 13 was prepared as follows :
0.02 mole of phenylethylselenocyanate in 50 ml of methanol was admixed with a solution of 0.5 g of sodium in 20 ml of methanol. The mixture was refluxed for 2 hours and an oil formed. After dilution with 75 ml of water, the mixture was extracted with ether. The ether extract was dried over sodium sulphate, filtered and concentrated by evaporation. Yield : 1.7g of yellow oil.

The phenylethylsenocyanate used was prepared refluxing with stirring for 6 hours a mixture of 0.1 mole of bromethylbenzene and 0.1 mole of potassium selenocyanate in 100 ml of acetone. The potassium bromide formed was filtered off by suction and the filtrate concentrated by evaporation. The residual oil was distilled under reduced pressure. Yield : 18 g.

The compounds according to the present invention are generally incorporated into the silver halide emulsion layer of the light-sensitive material. The way in which the compounds of use according to the invention are added to the emulsions is not critical and the addition can be made during no matter what step of emulsion preparation; they can be added before or after the emulsion has been optically sensitized, preferably just before coating of the emulsion on a suitable support such as for example paper, glass or film.

Instead of incorporating the compounds of the invention into the emulsion layer they can also be incorporated into another layer of the photographic material, e.g. a gelatin antistress layer or intermediate layer, which is in water-permeable relationship with the said emulsion layer.

The compounds of use according to the present invention may be incorporated into any type of light-sensitive material comprising a silver halide emulsion layer e.g. a spectrally sensitized or non-sensitized silver halide emulsion layer, a silver halide emulsion layer of use in diffusion transfer processes for the production of silver images, an X-ray emulsion layer, and an emulsion layer sensitive to infra-red radiation. They may be incorporated into high speed negative material as well as into rather low speed positive materials. Various silver salts may be used as light-sensitive salt e.g. silver bromide, silver iodide, silver chloride, or mixed silver halides e.g. silver chlorobromide or silver bromo-iodide.

The silver halides are dispersed in the common hydrophilic colloids such as gelatin, casein, zein, polyvinyl alcohol, carboxymethylcellulose, alginic acid, etc., gelatin being, however, favored.

The amount of compound according to the present invention employed in the light-sensitive silver halide material depends on the particular type of emulsion and the desired effect and can vary within very wide limits. The optimum amount to be added is best determined for each particular type of emulsion by trial.

When used as antifoggant, the most suitable concentration of compound according to the present invention is generally comprised between 0.01 millimole and 1 millimole, preferably between 0.05 millimole and 0.25 millimole per mole of silver halide. When used as antibronzing agent the compounds according to the present invention are preferably used in amounts from some mg to about 500 mg per sq.m. of light-sensitive printing material.

The light-sensitive emulsions may be chemically as well as optically sensitized. They may be chemically sensitized by effecting the ripening in the presence of small amounts of sulphur containing compounds such as allyl thiocyanate, allyl thiourea, sodium thiosulphate, etc. The emulsions may also be sensitized by means of reductors for instance tin compounds as described in our British Patent Specification 789,823 and small amounts of noble metal compounds such as gold, platinum, palladium, iridium, ruthenium and rhodium.

Furthermore, the emulsions may also comprise compounds which sensitize the emulsion by development acceleration for example alkylene oxide polymers. These alkylene oxide polymers may be of various type. Various derivatives of alkylene oxides may be used to sensitize the silver halide emulsions e.g. alkylene oxide condensation products as described among others in U.S. Pat. Nos. 2,531,832 and 2,533,990 in U.K.Patent Specifications 920,637, 940,051, 945,340 and 991,608 and in Belgian Patent Specification 648,710. Other compounds that sensitize the emulsion by development acceleration and that are suitable for use in combination with the compounds of use according to the invention are the onium derivatives of amino-N-oxides as described in U.K.Patent Specification 1,121,696.

In conjunction with light-sensitive materials comprising compounds according to the above general formula there may also be used known stabilizers for instance heterocyclic nitrogen containing thioxo compounds such as benzothiazoline-2-thione and 1-phenyl-Δ_2-tetrazoline-5-thione, mercury compounds such as those described in Belgian Patent Specifications 524,121 and 677,337 and in published Dutch Patent Application 67 15 932 and compounds of the hydroxytriazolopyrimidine type (hydroxyazaindolizines), particularly in extreme storage and development circumstances.

Other addenda such as hardening agents, wetting agents, plasticizers, color couplers, developing agents and optical sensitizers can be incorporated into the emulsion in the usual way.

The following examples illustrate the stabilizing or fog-inhibiting action of compounds corresponding to the above general formula. In these examples, the values I and II given for the speed are exposure values corresponding with density 0.1 above fog and density 1 above fog respectively; a decrease of the value by 30 means a doubling of the speed.

Example 1

A conventional photographic gelatino silver bromo-iodide emulsion (4.5 mole percent iodide) comprising per kg an amount of silver halide equivalent to 50 g of silver nitrate was divided into two portions A and B. To emulsion portion B was added per kg of emulsion 0.03 mmole of compound 2. Then the emulsions were coated on a conventional support and dried.

The values of speed, gradation and fog of the materials formed were determined shortly after preparation and after incubation for 5 days at 57°C and 34 percent

relative humidity. The values obtained are listed in the table below.

Development occurred at 20°C for 5 min. in a developing solution having the following composition :

water	800 ccs
p-monomethylaminophenol sulphate	1.5 g
sodium sulphite (anhydrous)	50 g
hydroquinone	6 g
sodium carbonate (anhydrous)	32 g
potassium bromide	2 g
water to make	1000 ccs

TABLE

Material	Fresh material				Incubated material			
	fog	grad-ation	speed I	II	fog	grad-ation	speed I	II
A	0.07	1.70	96	175	0.59	1.52	93	178
B	0.07	1.58	102	184	0.23	1.41	78	171

Example 2

Example 1 was repeated with the difference that the emulsion was divided into three aliquot portions to which the compounds listed in the table below were added in the concentration given. The sensitometric results obtained are listed in the following table.

Compound added per kg of emulsion	fresh material				incubated material			
	fog	grad-ation	speed I	II	fog	grad-ation	speed I	II
none	0.13	1.52	52	144	0.77	1.11	69	172
0.03 millimole of compound 4	0.11	1.47	55	149	0.43	1.31	57	156
0.03 millimole of compound 3	0.11	1.39	54	152	0.45	1.17	54	159

Example 3

A gelatino silver bromoiodide emulsion (2 mole percent of iodide) comprising per kg an amount of silver halide equivalent to 100g of silver nitrate was divided into three aliquot portions. To each portion, one of the compounds listed in the table below was added in the concentration given.

The emulsions were coated on a cellulose triacetate support provided with a subbing layer and dried.

The materials were stored for 5 days at 57°C and 34 percent of relative humidity whereupon they were exposed to X-rays with an X-ray radiation source of 80 kV and developed for 8 min. at 20°C in a common X-ray developer having the following composition :

water	800 ccs
p-monomethylaminophenol hemisulphate	4 g
hydroquinone	10 g
anhydrous sodium sulphite	65 g
anhydrous sodium carbonate	45 g
potassium bromide	5 g
water up to	1000 ccs

The values of the fog produced in the stored materials as compared with the values of the fog produced in the freshly prepared materials are listed in the following table.

Compound added per kg of emulsion	fog in fresh materials	fog in stored materials
none	0.19	1.99
0.2 mmole of compound 4	0.09	0.34
0.6 mmole of compound 11	0.05	0.05

Example 4

A gelatino silver bromoiodide emulsion as described in example 3 was divided into four aliquot portions. To each portion, one of the compounds listed in the table below was added in the concentration given.

The emulsions were then further treated as described in example 3 and the resulting materials were conditioned in a moist atmosphere of about 60 percent of relative humidity. Thereupon the materials were packed in aluminum laminated paper and stored for 5 days at 57°C.

The values of the fog produced in the stored materials as compared with the values of the fog produced in the freshly prepared materials are listed in the following table.

Development occurred as described in example 3.

compound added per kg of emulsion	fog produced in fresh materials	fog produced in stored materials
none	0.19	2.47
0.2 mmole of compound 4	0.09	0.28
0.6 mmole of compound 11	0.05	0.05

The following examples illustrate the antibronzing action of the compounds corresponding to the above general formula in photographic printing material.

Example 5

Material 1

A gelatino silver chloroiodide emulsion (0.4 mole percent of iodide), prepared with a proportion of silver nitrate to gelatin of 1 to 3 was applied to a baryta-coated paper support in such a way that after drying an amount of silver halide, equivalent to 1.9 g of silver nitrate was present per sq.m of light-sensitive material. The light-sensitive emulsion layer was overcoated with a thin gelatin covering layer which was hardened afterwards.

Material 2

Material 2 was prepared as material 1 with the difference, however, that per kg of light-sensitive emulsion ready for coating, 1.8 mmol of compound 9 was added from a solution in ethylene glycol monomethyl ether.

Material 3

Material 3 was prepared as material 1 with the difference, however, that per kg of light-sensitive emulsion ready for coating, 1.8 mmol of compound 10 was added from a solution in ethylene glycol monomethyl ether.

Material 4

Material 4 was prepared as material 1 with the difference, however, that per kg of light-sensitive emulsion ready for coating, 1.8 mmol of compound 11 was added from a solution in ethylene glycol monomethyl ether.

Material 5

Material 5 was prepared as material 1 with the difference, however, that per kg of light-sensitive emulsion ready for coating, 1.8 mmol of compound 3 was added from a solution in isopropylalcohol.

Strips of each of these materials were exposed and developed for 5 minutes at 20°C in a bath of the following composition :

water	800 ccs
p-monomethylaminophenol sulphate	1.5 g
anhydrous sodium sulphite	50 g
hydroquinone	6 g

anhydrous sodium carbonate	32 g
potassium bromide	2 g
water up to	1000 ccs

The strips were rinsed and then fixed for 5 minutes at room temperature in the following composition

water	800 ccs
anhydrous sodium thiosulphate	120 g
potassium metabisulphite	25 g
water to make	1000 ccs

The strips were then pressed for 6 minutes with their light-sensitive side to a polished plate of 80°C.

The density of the various material strips was measured with a Macbeth densitometer before as well as after hot-glazing. The following results were attained.

	Density before hot-glazing	Density after hot-glazing
1st test		
material 1	2.04	1.59
material 2	2.05	1.96
2nd test		
material 1	1.96	1.67
material 3	1.99	1.86
3rd test		
material 1	1.98	1.64
material 4	2.01	1.89
material 5	1.96	1.82

Example 6

Material 1

A gelatino silver bromochloride emulsion (46 mole percent of chloride), prepared with a proportion of silver nitrate to gelatin of 1 to 3 was applied to a baryta-coated paper support in such a way that after drying an amount of silver halide, equivalent to 2.6 g of silver nitrate was present per sq.m of light-sensitive material. The light-sensitive emulsion layer was overcoated with a thin gelatin covering layer which was hardened afterwards.

Material 2

Material 2 was prepared as material 1 with the difference, however, that per kg of light-sensitive emulsion ready for coating, 1.8 mmol of compound 9 was added from a solution in ethylene glycol monomethyl ether.

Material 3

Material 3 was prepared as material 1 with the difference, however, that per kg of light-sensitive emulsion ready for coating, 1.8 mmol of compound 10 was added from a solution in ethylene glycol monomethyl ether.

Material 4

Material 4 was prepared as material 1 with the difference, however, that per kg of light-sensitive emulsion ready for coating, 2.4 mmol of compound 11 was added from a solution in ethylene glycol monomethyl ether.

Material 5

Material 5 was prepared as material 1 with the difference, however, that per kg of light-sensitive emulsion ready for coating, 2.4 mmol of compound 3 was added from a solution in isopropyl alcohol.

Strips of each of these materials were further treated as described in example 5.

The following results were attained.

	Density before hot-glazing	Density after hot-glazing
1st test		
material 1	1.85	1.70
material 2	1.87	2.00
2nd test		
material 1	1.84	1.76
material 3	1.78	1.84
3rd test		
material 1	1.84	1.68
material 4	1.83	1.93
material 5	1.81	1.78

Example 7

Material 1

A gelatino silver bromochloroiodide emulsion (9 mole percent of chloride and 1 mole percent of iodide), prepared with a proportion of silver nitrate to gelatin of 1 to 1.8 was applied to a baryta-coated paper support in such a way that after drying an amount of silver halide, equivalent to 2.5 g of silver nitrate was present per sq.m of light-sensitive material. The light-sensitive emulsion layer was overcoated with a thin gelatin covering layer which was hardened afterwards.

Material 2*a*

Material 2*a* was prepared as material 1 with the difference, however, that per kg of light-sensitive emulsion ready for coating, 0.6 mmol of compound 9 was added from a solution in ethylene glycol monomethyl ether.

Material 2*b*

Material 2*b* was prepared as material 1 with the difference, however, that per kg of light-sensitive emulsion ready for coating, 1.8 mmol of compound 9 was added from a solution in ethylene glycol monomethyl ether.

Strips of each of these materials were further treated as described in example 5.

The following results were attained :

	Density before hot-glazing	Density after hot-glazing
1st test		
material 1	1.90	1.82
material 2*a*	1.92	1.95
material 2*b*	1.87	2.08

We claim:

1. Photographic material comprising a support and at least one light-sensitive silver halide emulsion layer comprising in said emulsion layer and/or in at least one water-permeable layer coated at the same side of the support as the said emulsion layer and being in water-permeable relation with said emulsion layer, at least one compound corresponding to the following general formula:

$$R_1—Q—Se—R_2$$

wherein:

Q stands for selenium or sulphur, and

each of R_1 and R_2 (the same or different) stands for an alkyl group, an aralkyl group or an aryl group;

said compound being present in a stabilizing amount or in an amount effective to inhibit fogging or bronzing.

2. Photographic material according to claim 1, wherein said material also comprises a stabilizer of the hydroxytriazolo-pyrimidine type.

3. Photographic material according to claim 1, wherein said material also comprises a development accelerator of the polyoxyalkylene type.

4. Photographic material according to claim 1, wherein said emulsion layer is a gelatino silver halide emulsion layer.

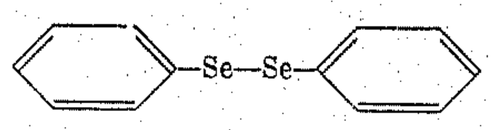
5. Photographic material according to claim 1 wherein Q is Se.

6. Photographic material according to claim 1 wherein Q is S.

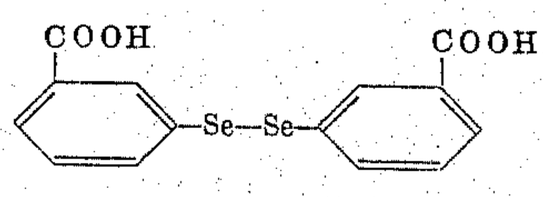
7. Photographic material according to claim 1 wherein R_1 and R_2 are alkyl.

8. Photographic material according to claim 1 wherein R_1 and R_2 are aryl.

9. Photographic material according to claim 1 wherein said compound has the formula:



10. Photographic material according to claim 1 wherein said compound has the formula:



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UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,728,126

DATED : April 17, 1973

INVENTOR(S) : Robert Joseph POLLET ET AL

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the heading, [30] Foreign Application Priority Data, "July 3, 1969" should read -- March 7, 1969 --.

Signed and Sealed this

Seventeenth Day of May 1977

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks