

[72] Inventors **Harald Huckstadt**
Cologne-Stammheim;
Wolfgang Himmelmann, Cologne-
Stammheim; Wilhelm Saleck, Schildgen,
Bergisch-Gladbach; August Randolph,
Leverkusen; Erwin Ranz, Leverkusen;
Walter Simmler, Odenthal; Hans-Dietrich
Golitz, Cologne-Stammheim, all of
Germany

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[73] Assignee **Agfa-Gevaert Aktiengesellschaft**
Leverkusen, Germany

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104, 94

[56] **References Cited**

UNITED STATES PATENTS

3,471,296 10/1969 Huckstadt et al..... **96/107**

Primary Examiner—William D. Martin
Assistant Examiner—Theodore G. Davis
Attorney—Connolly and Hutz

[54] **PHOTOGRAPHIC SILVER HALIDE EMULSION**
WITH INCREASED SENSITIVITY
7 Claims, No Drawings

ABSTRACT: A photographic silver halide emulsion chemically sensitized by a cyclic amino compound containing at least one dialkylsilyl group added to the silver halide emulsion.

PHOTOGRAPHIC SILVER HALIDE EMULSION WITH INCREASED SENSITIVITY

The invention relates to photographic silver halide emulsions chemically sensitized by the addition of cyclic amine compounds containing at least one dialkylsilyl group.

A number of methods have been described for improving the sensitivity of photographic silver halide emulsions other by optical or spectral sensitization through the incorporation of certain sensitizing dyes in the emulsion. The incorporation of such dyes in the emulsion increases the optical or spectral range of sensitivity, and for this reason such dyes are commonly referred to as optical or spectral sensitizing dyes. Contrary to such optical or spectral sensitizers the so-called chemical sensitizers are believed to react with silver halide to form, on the surface of the silver halide grain, sensitivity specks the chemical nature of which depends on the kind of the chemical sensitizer. The sensitivity of silver halide emulsions can be increased by chemical ripening or afterripening during the preparation of the emulsion, by either prolonging the ripening time or by the addition of suitable substance such as compounds of noble metals or thiosulfate or other sulfur compounds. According to another method customarily employed the sensitivity of a photographic emulsion can be increased by the addition of development accelerators or chemical sensitizers to the emulsion usually when it is completely ripened.

Suitable development accelerators are, for example, compounds containing onium groups (for example, quaternary ammonium or phosphonium and ternary sulfonium salts) and polyalkylene oxides and derivatives of polyalkylene oxides.

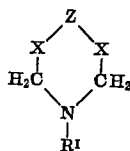
The process of chemical sensitization, however, reaches a limit beyond which further addition of sensitizing compounds or of prolonged digestion in the presence of a sensitizer, merely increases the undesired fog of the photographic emulsions.

In particular with respect to polyalkylene oxide sensitizers, many attempts have been made to increase the sensitizing action by modifying the chemical structure or by using them in combination with other compounds. However, in practice, none of these compounds completely meet the requirements as regards producing a satisfactory increase in sensitivity without concomitant increases in fog or poor keeping qualities.

It is an object of the present invention to provide chemical sensitizers for photographic silver halide emulsions. Another object is to increase the sensitivity of ordinary photographic silver halide emulsions without concomitant increases in fog or poor keeping qualities to a degree which might seriously affect the usefulness of the emulsion.

We now have found that excellent increases in sensitivity can be achieved with little or no fogging by addition of cyclic amino compounds containing at least one dialkylsilyl group to silver halide emulsions.

Suitable compounds include those of the following formula:



wherein represents:

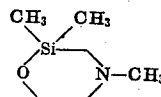
Z = oxygen or the group NR^1 ; X = a methylene or a dialkylsilyl group in which the alkyl groups preferably contain up to three carbon atoms, in particular dimethylsilyl;

R¹ = a saturated or olefinically unsaturated aliphatic group containing up to 18, and preferably up to 12, carbon atoms, which group may be substituted with any photographically acceptable substituted, e.g., with hydroxyl, amino, alkyl-amino or dialkylamino, cyan, alkylthio, alkoxy, dialkylsilyl or alkylsilylhydroxy groups;

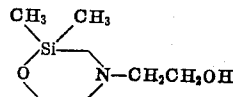
R'' = an alkyl group containing up to six carbon atoms, the compound containing at least one dialkylsilyl group, in particular a dimethylsilyl group.

Particular utility is exhibited by the following compounds:

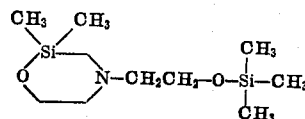
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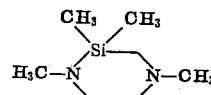
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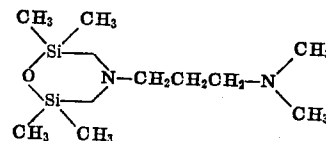
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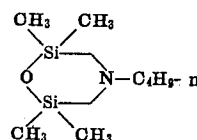
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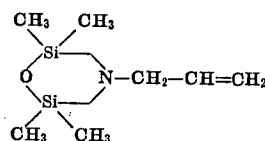
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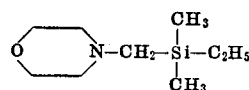
VI.



VII.



VIII.



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The preparation of these compounds is described in "Chemische Berichte" 94, (1961), pp. 1585-1591 and 96, 75 (1963), pp. 349-356.

Those substances which are used according to the invention and which are silamorpholines ($7=0$) are stable to hydrolysis. Silapiperazines ($7=>NRL$), which may also be used are less stable to hydrolysis and presumably, if they are used their hydrolysis products are also effective.

The compounds according to the invention can be used in any silver halide emulsions. Silver halides which may be used are silver chloride, silver bromide or mixtures thereof, if desired with a small amount of silver iodide of up to 10 mols percent. The silver halides can be dispersed in the usual hydrophilic compounds, for example, in carboxymethyl cellulose, polyvinyl alcohol, polyvinyl pyrrolidone, alginic acid and its salts, esters or amides, and preferably in gelatin.

The preparation of photographic silver halide emulsions includes 3 separate steps:

1. emulsification and physical ripening which is also called Ostwald ripening;
2. the freeing of the emulsion of excess water-soluble salts, usually by washing with water and drying, and
3. the afterripening which is also called chemical ripening to obtain increased emulsion speed or general sensitivity.

The sensitizer of the present invention can be added to the emulsion before, during or after the chemical ripening or they can be added immediately prior to the casting. In many cases it has proved advantageous to add the chemical sensitizer of the present invention before or during the afterripening.

The particular quantity of the sensitizers of the invention used in a given emulsion can vary, depending upon the effects desired, the silver content of the emulsion, the silver halide composition etc. The amount used is also dependent upon the particular state at which the sensitizer was added during the preparation of the emulsion. Generally they are added in amounts of 0.005 to 5 g. preferably 0.05 to 1 g. per liter of emulsion ready for casting.

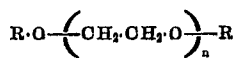
The sensitizers can be dissolved in water or a solvent miscible with water or a mixture of water and water miscible solvents, and added in such form to the emulsion. The solvent is not critical and should be selected so that it should have no harmful effect on the photographic properties of the silver halide emulsion.

The optimum amount for any sensitizer of the present invention can be determined for any particular emulsion by running a series of comparison tests in which the quantity of the sensitizer is varied over a given range. Exposure of the emulsion containing the sensitizer in a manner well-known and measuring of the sensitivity in conventional apparatuses will reveal most advantageous concentrations. Such technique is well understood by those skilled in the art.

The photographic emulsion in which the sensitizers according to the invention are used, can contain additional chemical sensitizers customarily employed. They can be sensitized, for example, with sulfur compounds as referred to, e.g., in the book "The Theory of the photographic Process," by Mees (1954), pages 149-161.

The emulsions can also be chemically sensitized with salts of noble metal such as gold, ruthenium, rhodium, palladium, iridium and platinum, used in amounts below that which produce any substantial fog. Representative compounds are ammonium chloropalladate, potassium chloroplatinate, potassium chloroaurate, auric trichloride and the like. The emulsions can be sensitized with reducing agents, stannous salts or polyamines and the like.

According to a preferred embodiment of the invention, the spirocyclic quaternary salts are used in combination with chemical sensitizers of the polyalkylene oxide type. Suitable compounds of this type are, for example, those of the following formula:



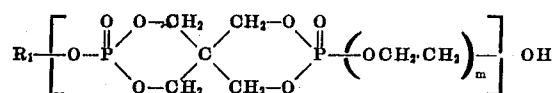
wherein R = denotes a hydrogen atom or an alkyl group with preferably up to 18 carbon atoms such as an ethyl or dodecyl, an acyl group, preferably an acyl radical of an aliphatic carboxylic acid having up to 18 carbon atoms such as

lauric acid or oleic acid, or an aryl group such as phenyl or p-dodecylphenyl;

n = an integer between 8 and 200. The ethylene oxide groups $CH_2 \cdot CH_2 \cdot O$ may be substituted for instance with alkyl having up to 18 carbon atoms. Molecular weights of from 1,500 to 10,000 are preferred for the polyethylene oxides, examples of which are described in U.S. Pats. Nos. 2,240,472 and 2,400,532.

Other suitable chemical sensitizers are derivatives of phosphoric acid which contain polyalkylene oxide chains. Suitable products have been described in British Pat. Nos. 1,045,183 and 1,045,184 or French Pat. Nos. 1,396,860 and 1,423,680.

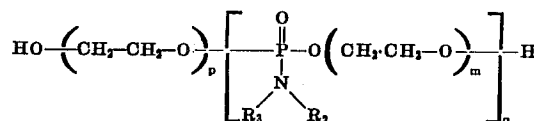
Such compounds are condensation products of spirocyclic pentaerythritol-di-phosphoric acid monohalides and polyethylene glycols containing about three to 100 ethylene oxide units in the molecule. They correspond to the following formula:



wherein R_1 = a hydrogen atom or an alkylene oxide chain having 3 to 100 alkylene oxide units;

m = an integer from 3 to 100 and Y = an integer from 1 to 10.

This group of chemical sensitizers also include the condensation products of amidophosphoric acid derivatives and polyethylene glycols of the above-mentioned type. Such compounds are represented by the following formula:



wherein R_2 = a hydrogen atom, an alkyl, aryl or aralkyl group and R_3 = an alkyl, aryl or aralkyl group;

R_2 and R_3 may together represent the ring members required for completing a 5- or 6-membered heterocyclic ring;

m = is an integer between 2 and 100 preferably between 3 and 50;

p = an integer from 0 to 100 and q = an integer from 1 to 5.

The spirocyclic quaternary salts according to the invention may also be used advantageously in combination with the cross linked or noncross linked water-soluble quaternated products of tertiary polyamines with bifunctional polyalkylene oxide derivatives. These quaternated products have been described in German Pat. application A 50 595 IXa 57 b.

The accelerators according to the invention may also be used in combination with the morpholine or thiomorpholine derivatives described in French Pat. Nos. 1,506,230 and 1,548,191. The accelerators described in the published Dutch applications 6,614,230 and 6,711,152 are also highly effective.

Furthermore, the emulsions may contain stabilizers such as homoopolar or salt-type compounds of mercury which contain aromatic or heterocyclic rings (e.g., mercaptotriazoles), simple mercury salts, sulfonium-mercury double salts and other mercury compounds. Other suitable stabilizers are azaindenes, preferably tetra or pentaazaindenes, especially those substituted with hydroxyl or amino groups. Such compounds have been described by Birr, Z. Wiss. Phot., 47, 2-58 (1952). Other suitable stabilizers include heterocyclic mercapto compounds such as phenylmercapto-tetrazole, quaternary benzthiazole derivatives and benztriazoles.

65	Sensitizer	Quantity g./kg. of emulsion	Relative sensitivity	γ	Fog
° DIN					
70	sensitizer		control	0.53	0.06
	A	0.48	+3.0	0.54	0.07
	VIII	0.24	+0.5	0.63	0.06
	VIII	0.24			
75	sensitizer				
	A	0.48	+3.5	0.55	0.06

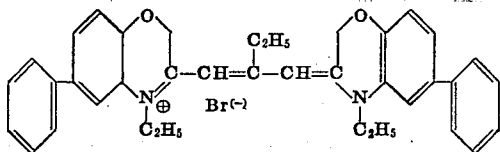
			control	0.65	0.06
sensitizer					
A	0.48	+2.0	0.55	0.06	
V	0.12	+1.0	0.60	0.05	
sensitizers					
A	0.48				
V	0.12	+3.0	0.63	0.14	
VI	0.12	+2.0	0.59	0.08	
sensitizers					
A	0.48				
VI	0.12	+3.0	0.59	0.18	
sensitizer		control	0.59	0.06	
B	0.48	+1.5	0.69	0.06	
V	0.24	+1.0	0.66	0.12	
V	0.24				
+ sensitizer					
B	0.48	+2.0	0.61	0.12	
sensitizer		control	1.20	0.09	
B	0.48	+1.0	1.20	0.13	
VI	0.24	+1.0	1.20	0.13	
VI	0.24				
+ sensitizer					
B	0.48	+2.0	1.11	0.15	
sensitizer		control	0.67	0.05	
B	0.48	+1.0	0.60	0.08	
III	0.12	+0.5	0.61	0.04	
III	0.12				
+ sensitizer					
B	0.48	+2.0	0.59	0.06	
sensitizer		control	1.25	0.10	
B	0.48	+1.5	1.18	0.14	
VIII	0.24	+1.0	1.29	0.09	
VIII	0.24				
+ sensitizer					
B	0.48	+3.0	1.05	0.13	

* The development time in this series of experiments was 16 minutes.

EXAMPLE 3

To a mixed emulsion which is composed of 90 percent of a silver iodobromide gelatin and 10 percent of a silver iodochlorobromide emulsion which has been chemically ripened to a maximum sensitivity in known manner with gold and sulfur compounds are added the following ingredients per liter of emulsion:

- 15 g. of 1-(3'-sulfo-4'-phenoxy)-phenyl-3-heptadecyl-pyrazolone as magenta coupler
- 250 mg. of 1,3,3a, 7-(4-hydroxy-6-methyl)-tetraazaindene as stabilizer
- 20 ml. of an aqueous 5 percent solution of saponin as wetting agent
- 2.5 ml. of an aqueous 30 percent solution of formaldehyde as hardener and
- 45 mg. of the green sensitizer of the following formula



The above emulsion is divided into 20 equal parts and the sensitizer shown in table 3 are added per liter of emulsion to the individual samples.

The samples are on a cellulose acetate support and dried. They are then exposed behind a step wedge and processed in the usual manner. Processing is carried out as follows:

Color-forming development	7 minutes
stop bath	5 minutes
rinsing	5 minutes
bleaching bath	5 minutes
rinsing	5 minutes
fixing bath	5 minutes
rinsing	10 minutes

The processing baths have the following composition:

Color-forming developer	
Diethyl-p-phenylenediamine sulfate	2.75 g.
hydroxylamine sulfate	1.20 g.
sodium sulfite anhydrous	2.00 g.
sodium hexametaphosphate	2.00 g.
potassium carbonate anhydrous	75.00 g.
potassium bromide	2.00 g.
make up to 1 liter	
Stop bath	
Sodium acetate	30.00 g.
acetic acid	6.00 g.
make up with water to 1 liter	
Bleaching bath	
Potassium ferricyanide	100.00 g.
potassium bromide	20.00 g.
acetic acid	4.00 g.
make up with water to 1 liter	
Fixing bath	
Sodium thiosulfate	200.00 g.
make up with water to 1 liter	

The color density of the magenta layers was determined with a "Macbeth Quanta Log, Model TD 102" densitometer, interposing the green filter into the path of the beam of measuring light.

The results of the sensitometric tests are shown in the following table 3.

Table 3

Sensitizer	Quantity g./kg. of emulsion	Relative sensitivity * DIN	γ	Fog
		control	0.70	0.10
II	0.3	+2.8	0.64	0.11
II	1.0	+2.8	0.68	0.12
II	3.0	+3.0	0.72	0.12
		control	0.64	0.18
I		+0.5	0.66	0.25
I	1.0	+2.6	0.64	0.26
I	3.0	+1.0	0.64	0.28
		control	0.45	0.15
V	0.3	+0.4	0.51	0.12
V	1.0	+1.2	0.34	0.15
V	3.0	+0.2	0.22	0.15
		control	0.42	0.12
VI	0.3	+3.2	0.42	0.16
VI	1.0	+4.0	0.48	0.17
VI	3.0	+2.8	0.44	0.25
		control	0.53	0.14
III	0.3	+0.8	0.54	0.14
III	1.0	+2.6	0.50	0.14
III	3.0	+0.8	0.47	0.10

EXAMPLE 4

The silver iodobromide gelatin emulsion of example 1 is divided into 13 equal parts and the substances specified in the following table, table 4, are added. The emulsion is applied onto a support and dried as in example 1 and developed for 6

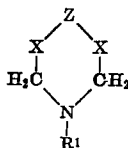
minutes at 20° C. in the developer given in example 2. Sensitizers A and B have the formulae given in example 2.

Table 4

Sensitizer	Quantity g./kg. of emulsion	Relative Sensitivity DIN	γ	Fog
A	0.480	control	0.92	0.21
B	0.480	+2.0	1.13	0.31
III	0.240	+1.5	0.96	0.28
		+2.0	0.97	0.24
III	0.240			
and A	0.480			
and B	0.480	+4.2	1.07	0.28
VIII	0.120	+1.8	1.02	0.24
VIII	0.120			
and A	0.480			
and B	0.480	+4.4	1.12	0.26
A	0.480	control	0.90	0.15
B	0.480	+2.0	1.06	0.11
V	0.120	+1.4	0.92	0.10
		+1.80	0.97	0.18
V	0.120			
and A	0.480			
and B	0.480	+3.1	1.10	0.40
VI	0.120	+2.3	1.01	0.16
VI	0.120			
and A	0.480			
and B	0.480	+3.7	1.10	0.30

We claim:

1. A light-sensitive silver halide emulsion which contains a sensitivity increasing amount of a chemical sensitizer of the following formula:



wherein

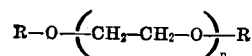
Z represents oxygen or the group NR'';
R' stands for a saturated or olefinically unsaturated aliphatic group containing up to 18 carbon atoms;
X is a methylene or a dialkylsilyl group;
R'' represents an alkyl group containing up to six carbon atoms, the sensitizer containing at least one dialkylsilyl group.

2. The emulsion of claim 1, wherein at least one of the group X represents a dialkylsilyl group, in which the alkyl groups have up to three carbon atoms.

3. The emulsion of claim 2, wherein at least one of the group X is a dimethylsilyl group.

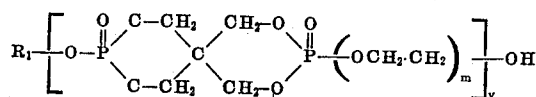
4. The emulsion of claim 1, which contains in addition a polyalkylene oxide sensitizer.

5. The emulsion of claim 4, which contains in addition a polyethylene oxide sensitizer of the following formula:



in which R represents hydrogen, alkyl group containing up to 18 carbon atoms, acyl radical of an aliphatic carboxylic acid containing up to 18 carbon atoms or a phenyl group and n is an integer of between 8 and 200.

6. The emulsion of claim 4, which contains in addition a polyalkylene oxide sensitizer of the following formula:



in which R₁ represents hydrogen or an alkylene oxide chain with 3 to 100 alkylene oxide units, m is an integer of between 3 and 100 and y is an integer of between 1 and 10.

7. The emulsion of claim 4 which contains in addition an onium compound of the following formula:

