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3,558,314

PROCESS FOR INCREASING THE SENSITIVITY OF PHOTOGRAPHIC SILVER HALIDE EMULSIONS

Harald Hueckstaedt, Cologne - Stammheim, Wilhelm Saleck, Schildgen, Bergisch Gladbach, and Herbert Mueller and August Randolph, Leverkusen, Germany, assignors to Agfa-Gevaert Aktiengesellschaft, Leverkusen, Germany, a corporation of Germany

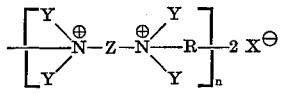
No Drawing. Filed Nov. 4, 1966, Ser. No. 591,974

Int. Cl. G03c 1/08, 5/26

U.S. Cl. 96—66.3 6 Claims

ABSTRACT OF THE DISCLOSURE

Light-sensitive silver halide material containing as a sensitizer a water soluble quaternary compound having the general formula:



wherein Y is a radical selected from the group consisting of alkyl, phenylalkyl, hydroxyalkyl, alkoxyalkyl, acyloxyalkyl, aminoalkyl, alkylaminoalkyl and acylaminoalkyl, the alkyl group of the radical having up to 18 carbon atoms; R and Z are divalent organic radicals, at least one of which is a polyalkylene oxide group, X is an anion and n is a number from 2 to 100 and a process for improving the sensitivity of a light-sensitive silver halide emulsion.

The invention relates to a process for increasing the sensitivity (speed) of photographic silver halide emulsions.

It is known that the sensitivity of photographic silver halide emulsions can be increased by the addition of so-called development accelerators or chemical sensitizers. Polyalkylene oxides, inter alia, have been described for this purpose.

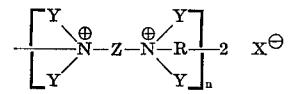
It is also known that, besides simple polyalkylene oxides of various chain lengths, polyalkylene oxides with onium substituents can be used as chemical sensitizers. A disadvantage inherent in almost all chemical sensitizers is the occurrence of a more or less pronounced chemical fog, which can limit the applicability of a development accelerator.

The invention therefore aims at finding substances that produce the least possible increase in fog while providing the greatest possible sensitivity-increasing effect on silver halide emulsions.

It has now been found that water-soluble quaternization products of tertiary polyamines with bifunctional polyalkylene oxide derivatives are eminently suitable as chemical sensitizers for photographic silver halide emulsions. The polymeric compounds to be used in the manner of the invention should preferably have an average

molecular weight of more than 2,000, specifically 10,000 to 250,000.

They include, in particular, polymeric compounds of the following formula:



where Y=alkyl with up to 18 C atoms, preferably with up to 5 C atoms, which can be substituted with phenyl, e.g., benzyl or phenylethyl, with hydroxyl such as β-hydroxyethyl, or with amino such as aminoethyl or aminopropyl; in this case the H atoms of the hydroxy or amino groups can also be substituted, e.g., with (1) acyl groups, in particular those that derive from aliphatic carboxylic acids with up to 18 C atoms, preferably with up to 5 C atoms, or from aromatic carboxylic acids, preferably benzenecarboxylic acids, such as acetyl, phenylacetyl, benzoyl, also carbamyl or N-alkyl or N-phenylcarbamyl, or (2) with alkyl radicals with up to 5 C atoms, which in their turn can be further substituted, e.g., with cyano, halo, hydroxy, or epoxy groups such as β-cyanoethyl, 3-chloro-2-hydroxypropyl, 2,3-epoxypropyl, and the like;

Z=a divalent organic radical, e.g., alkylene with up to 18 C atoms, preferably up to 5 C atoms, which can be interrupted by hetero atoms such as sulfur or, in particular, oxygen, e.g., diethyl ether groups, aralkylene such as benzyl or xylylene, also a polyalkylene oxide bridge with a chain length of preferably 3 to 300 alkylene oxide units; polyethylene oxide bridges that can in part contain units of propylene oxide or butylene oxide as well are preferred, however;

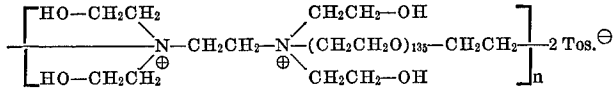
R=Z, preferably, however, a polyalkylene oxide group of the type mentioned above; at least R or Z must be a polyalkylene oxide group; compounds in which both Z and R are a polyalkylene oxide bridge, especially a polyethylene oxide bridge, are preferable.

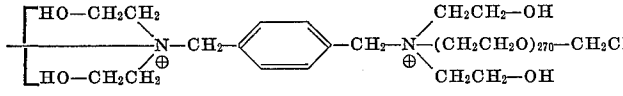
n=2–100, preferably 5–10;

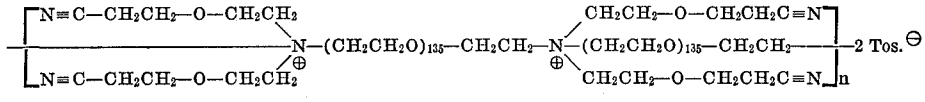
X=any anion; the chemical nature of the anion is of subordinate importance. The anion can be selected in conformity with the requirements of the production process. Halides, toluenesulfonates, methyl sulfates, and the like, for example, are suitable.

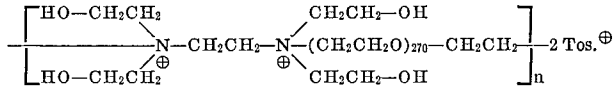
The compounds of the above formula can also be crosslinked, especially by way of the Y radical. This can occur, for example, when polymers of the given type, in which Y stands for an aminoalkyl or hydroxyalkyl group and an epoxy group or halogen radical, react with one another. A crosslinking is also achieved when polycondensates of the above formula, in which Y contains substituents with a Zerewitinoff-active hydrogen atom, are made to react with a diisocyanate such as hexamethylene diisocyanate.

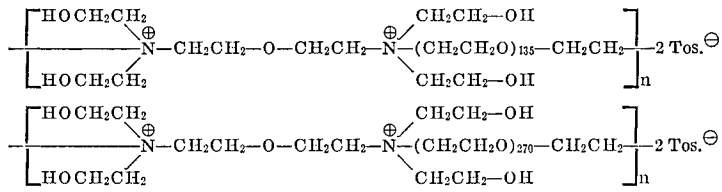
The following (wherein "TOS" signifies a toluene sulfonic acid moiety) may be cited as examples of the claimed compounds:

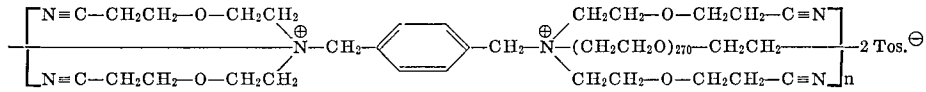
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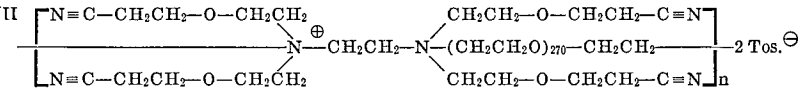
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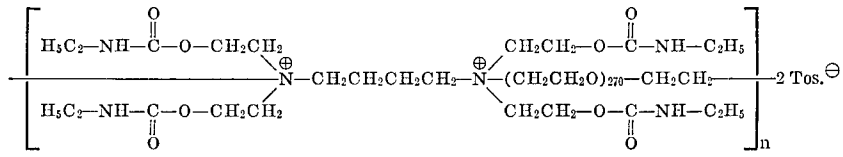
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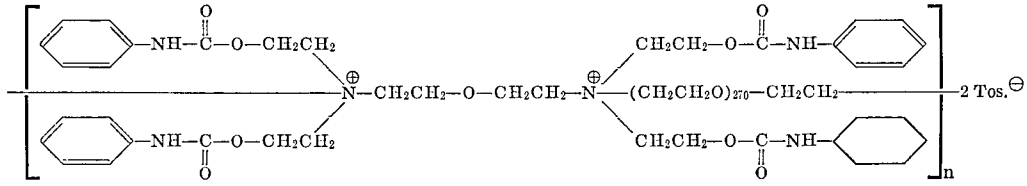
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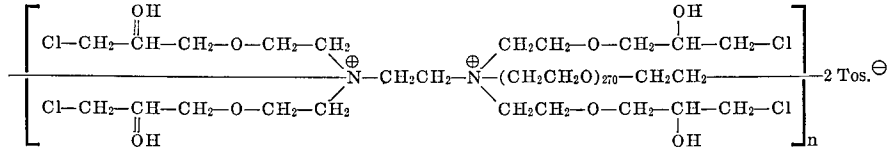
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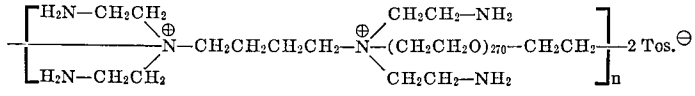
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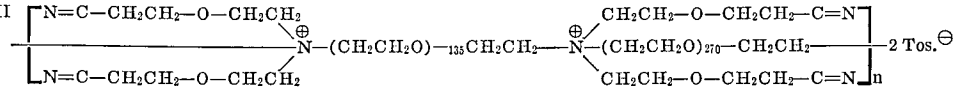
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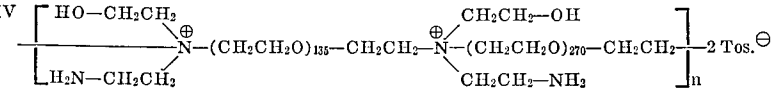
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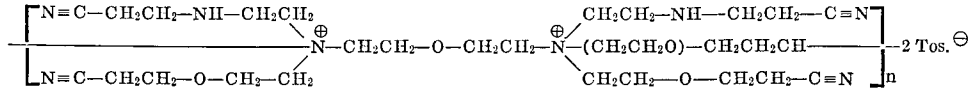
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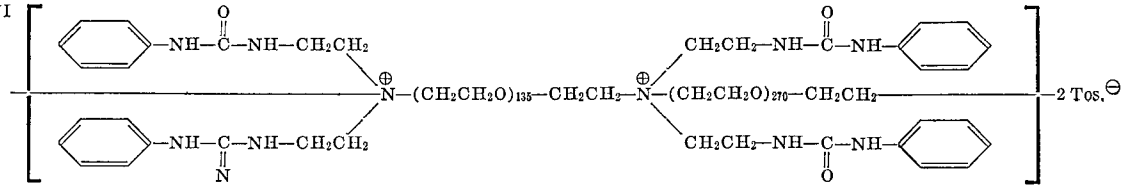
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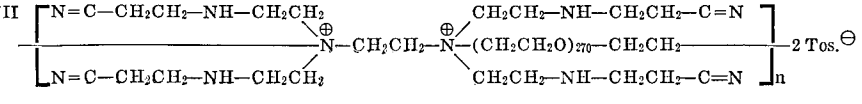
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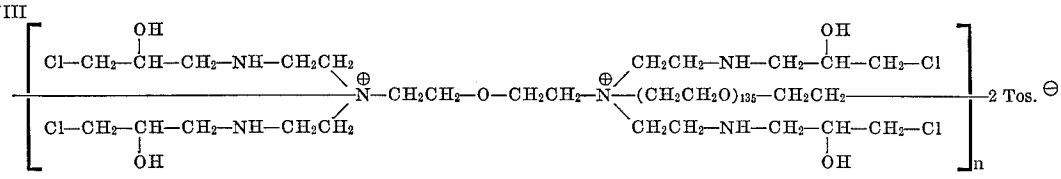
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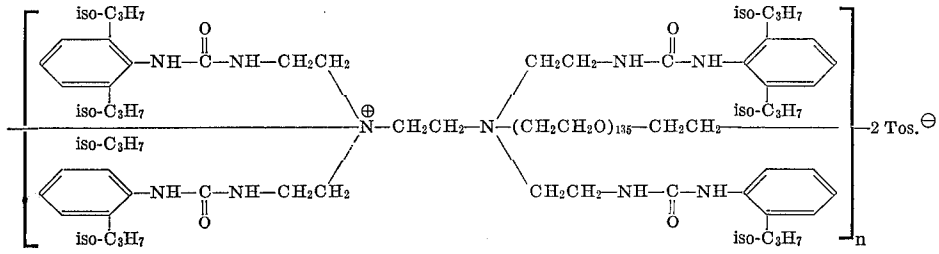
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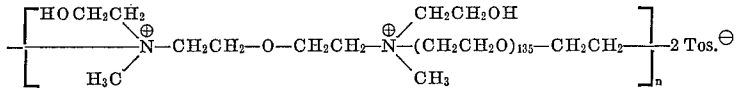
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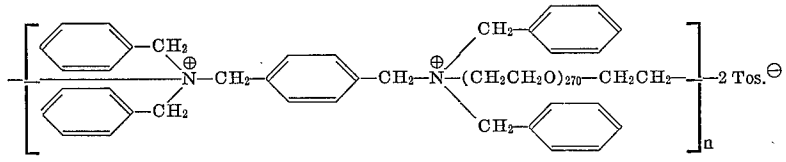
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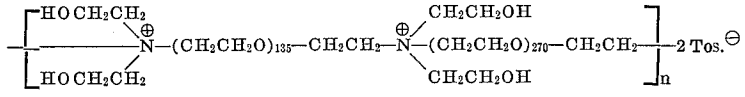
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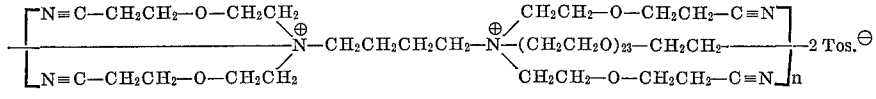
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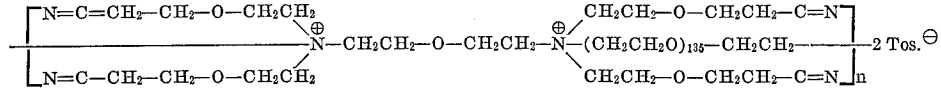
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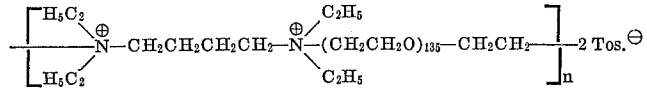
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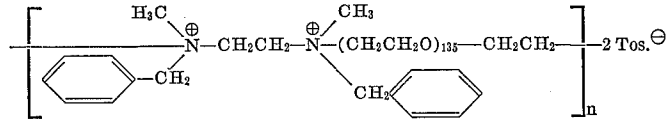
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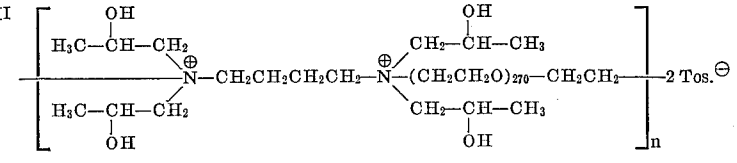
XXV



XXVI



XXVII



The production of the compounds to be used according to the invention may be explained with Substance VIII taken as an example, temperatures being in degrees centigrade:

Step 1

420 g. of diethanolamine and 160 g. of NaOH are dissolved in a liter of ethanol and the solution is heated to boiling. 198 g. of ethylene chloride is added dropwise at the boil while the solution is stirred. Next, the solution is refluxed for 2 hours and the alcohol is then distilled off. During the distillation the sodium chloride formed in the reaction precipitates out. To remove it, the distillation is interrupted and the material is cooled and filtered. At the end of the distillation, about 350 g. of a nondistillable and filterable oil remains behind.

Step 2

236 g. of the above described oil is dissolved in 500 ml. of water with 20 g. of NaOH added. 265 g. of acrylonitrile is added dropwise at 40–45° with stirring. Since the reaction is exothermic, with the proper rate of addition the prescribed temperature can be maintained without external application of heat. Next, the reaction mixture is stirred for 2 to 3 hours more at 40–45° and then neutralized with acetic acid. After the solution has been saturated with common salt, it is repeatedly extracted with methylene chloride. The extract is dried with sodium sulfate. After evaporation of the methylene chloride, about 250 g. of a thin oil that can no longer be distilled remains behind.

Step 3

1.27 g. of the compound made in Step 2 and 70 g. of a polyethylene oxide bistosylate (with 270 ethylene oxide units) are refluxed for 3 hours in 70 ml. of n-butanol. The solvent is then distilled off. A yellow to brownish wax is obtained in quantitative yield.

The other substances are prepared analogously. With some of them, the reaction product of secondary amine and bishalide (corresponding to Step 1) was reacted at the free-OH or -NH groups with isocyanates or epichlorohydrin and then quaternized.

The substances of the invention can be added to the photographic emulsion at any stage in its preparation, before, during, or after chemical ripening. They can also be added to the coating solution immediately before coating. The amount added depends on the effect desired and can be determined by one skilled in the art by the usual tests. Normally, amounts of 0.1 to 5 g. per mole of silver halide are sufficient.

The substances of the invention can be used in any silver halide emulsion. Suitable silver halides are silver chloride, silver bromide, or mixtures thereof, if desired with a small silver iodide content of up to 10 mole percent. The silver halides can be dispersed in common hydrophilic compounds, for example, in carboxymethylcellulose, polyvinyl alcohol, polyvinylpyrrolidone, alginic acid and its salts, esters or amides, or preferably, gelatin.

The emulsions can also contain other chemical sensitizers, e.g., quaternary ammonium and phosphonium as well as ternary sulfonium salts, reducing agents such as stannous salts, polyamines such as diethylene-triamine, or sulfur compounds such as described in U.S. Patent 1,574,944. For chemical sensitization, the specified emulsions can also contain salts of noble metals such as ruthenium, rhodium, palladium, iridium, platinum, or gold, as has been described in the article by R. Koslowsky in Z. Wiss. Phot. 46, 65–72 (1951).

The emulsions can also be optically sensitized, e.g., with the conventional polymethine dyestuffs such as neutrocyanine, basic or acid carbocyanines, rhodacyanines, hemicyanines, styryl dyestuffs, oxonols, and the like. Such sensitizers are described in F. M. Hamer's book, "The Cyanine Dyes and Related Compounds" (1964).

The emulsions can contain the usual stabilizers, e.g., homopolar or salt-type compounds of mercury with 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, in particular those that are substituted with hydroxy or amino groups. Such compounds are described in the article by Birr in Z. Wiss. Phot. 47, 2–58 (1952). Other suitable stabilizers are, inter alia, heterocyclic mercapto compounds, e.g., phenylmercaptotetrazole, quaternary benzothiazole derivatives, benzotriazole, and the like.

The emulsions can be hardened in the usual manner, e.g., with formaldehyde or halogen-substituted aldehydes that contain a carboxyl group, e.g., mucobromic acid, diketones, methanesulfonate, dialdehydes, and the like.

The compounds of the invention can also be added to emulsions containing color couplers.

In addition, they can be added to the developer as well as to an emulsion.

The way in which the new chemical sensitizers work will be explained more fully with the following examples, wherein percentages are by weight unless otherwise indicated, and temperatures are in degrees C.

EXAMPLE 1

600 mg. of saponin as wetting agent,

200 mg. of 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene as stabilizer, and

10 ml. of a 10% aqueous formaldehyde solution were added to a silver bromide-iodide gelatin emulsion containing, per kilogram of coating solution, 0.3 mole of silver halide with an iodine content of 6 mole-% referred to 1 mole of silver halide.

This emulsion was divided into 8 equal parts and the following substances were added to the individual parts:

Sample A: comparison sample—no addition

Sample B: 480 mg. of the chemical sensitizer of Example 1 in German Patent 1,178,297 per liter of emulsion

Sample C: 480 mg. of Compound VIII per liter of emulsion

Sample D: 480 mg. of Compound XXIII per liter of emulsion

Sample E: 480 mg. of Compound VII per liter of emulsion

Sample F: 480 mg. of Compound XXIV per liter of emulsion

Sample G: 480 mg. of Compound III per liter of emulsion

Sample H: 480 mg. of Compound IV per liter of emulsion

The above coating solutions were coated onto a cellulose acetate base.

All the samples were exposed to light in a sensitometer behind a gray step wedge and developed for 10 minutes in a developer of the following composition at 20°:

	G.
Sodium sulfite, anhydrous	70
Borax	7
Hydroquinone	3.5
p-Monomethylaminophenol	3.5
Sodium citrate	7
Potassium bromide	0.4

Water to make 1 liter.

The second three columns of the following table give the sensitometric values after three days' holding in a heating chamber at 60°.

TABLE 1

	10 minutes			3 days at 60° in a heating chamber, 20 minutes development		
Sample	Sensitivity	Gamma	Density	Sensitivity	Gamma	Density
A (Standard)	100	0.90	0.15	33	1.8	0.27
B	166	0.95	0.20	66	1.6	0.45
C	166	1.15	0.15	100	1.9	0.30
D	166	1.00	0.15	117	1.7	0.29
E	183	1.20	0.14	133	1.8	0.31
F	166	1.15	0.14	100	1.8	0.30
G	183	1.20	0.16	133	1.9	0.29
H	166	1.25	0.16	100	1.9	0.30

The sensitivity data are so selected that a value of 200 compared to the standard of 100 means twice the sensitivity (=1 stop). Conversely, the value 0 means half the sensitivity of the standard.

In another experiment, the same emulsion was divided into 5 equal parts, to which the following substances were added:

Sample A: comparison sample—no addition

Sample B: 480 mg. of the chemical sensitizer of Example 1 in German Patent 1,178,297 per liter of emulsion

Sample C: 480 mg. of Compound I per liter of emulsion

Sample D: 480 mg. of Compound VI per liter of emulsion

Sample E: 480 mg. of Compound XI per liter of emulsion

The coating samples were developed for 10 minutes in the same developer as in Table 1.

TABLE 2

Sample	10 minutes			3 days at 60° in a heating chamber, 20 minutes development		
	Sensitivity	Gamma	Density	Sensitivity	Gamma	Density
A (standard)	100	0.90	0.08	100	1.5	0.12
B	150	0.90	0.16	66	1.4	0.39
C	150	1.10	0.10	133	1.6	0.21
D	166	1.15	0.10	166	1.9	0.20
E	150	1.05	0.11	150	1.8	0.19

In another experiment, the same emulsion was divided into 5 parts and the following compounds were added to the parts:

Sample A: comparison sample—no addition

Sample B: 480 mg. of Compound XXV per liter of emulsion

Sample C: 480 mg. of Compound XIX per liter of emulsion

Sample D: 480 mg. of Compound IX per liter of emulsion

Sample E: 480 mg. of Compound X per liter of emulsion

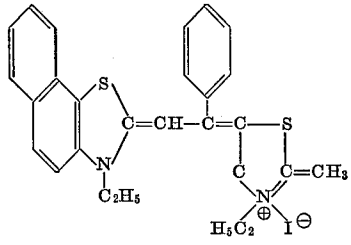
The coating samples were developed for 10 minutes in the same developer as in Table 1.

TABLE 3

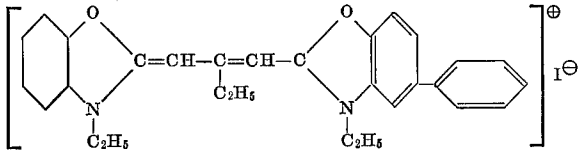
Sample	10 minutes			3 days at 60° in a heating chamber, 20 minutes development		
	Sensitivity	Gamma	Density	Sensitivity	Gamma	Density
A (standard)	100	1.00	0.09	50	1.6	0.19
B	150	1.05	0.10	100	1.8	0.21
C	183	1.10	0.09	133	1.7	0.24
D	150	1.15	0.10	100	2.0	0.26
E	166	1.05	0.11	133	1.9	0.20

EXAMPLE 2

40 mg. of the panchromatic sensitizer of the formula



and 20 mg. of the orthochromatic sensitizer of the formula



were added to the same emulsion as in Example 1, and the emulsion was divided into 7 equal parts. The following compounds were added to the individual parts.

Sample A: comparison sample—no addition

Sample B: 240 mg. of the chemical sensitizer of Example 1 in German Patent 1,178,297 per liter of emulsion

Sample C: 240 mg. of the Compound VIII per liter of emulsion

Sample D: 240 mg. of Compound VII per liter of emulsion

Sample E: 240 mg. of Compound IV per liter of emulsion

Sample F: 240 mg. of Compound V per liter of emulsion

Sample G: 400 mg. of Compound IV per liter of emulsion

The coating samples were developed 10 or 20 minutes in the same developer as in Example 1.

TABLE 4

Sample	10 minutes			20 minutes		
	Sensitivity	Gamma	Density	Sensitivity	Gamma	Density
A (standard)	100	0.70	0.02	100	1.20	0.05
B	217	0.75	0.05	217	1.30	0.08
C	217	0.80	0.02	217	1.40	0.06
D	217	0.80	0.02	233	1.30	0.05
E	217	0.75	0.02	217	1.25	0.05
F	217	0.75	0.02	217	1.20	0.06
G	233	0.80	0.02	217	1.30	0.06

It is evident from Tables 1–4 that the compounds of the invention are equal in sensitivity to and in part better than the previously customary polyethylene oxide derivatives, while fog is substantially less.

EXAMPLE 3

To a silver bromide negative emulsion that had been ripened in the conventional way with sulfur and gold compounds to maximum sensitivity, there was added a color coupler (1-(3'-sulfo-4'-phenoxy)-phenyl - 3 - heptadecyl pyrazolone), which gives a magenta image, as well as an optical sensitizer for the green spectral region.

Stabilizers, wetting agents, and hardeners such as are customary for photographic films were also added to the emulsion.

The emulsion thus prepared was divided into two parts before being coated onto a photographic base, and the parts were then treated further as follows:

Part A was coated on without any further addition (standard).

Part B received 1.3 g. of Compound VII per mole of silver halide before coating.

The two samples were exposed behind a step wedge and processed as follows:

	Minutes
Color developer	8
Stop bath	5
Rinsing	5
Bleaching bath	5
Rinsing	5
Fixing bath	5
Rinsing	10

The composition of the baths is given below:

	G.
Color developer:	
Sodium hexametaphosphate	2.0
Diethyl-p-phenylenediamine	2.5
Sodium sulfite	3.0
Hydroxylamine sulfate	1.2
Potassium carbonate	50.0
Potassium bromide	2.0
Water to make 1 liter.	
Stop bath:	
Sodium acetate	30.0
Glacial acetic acid	6.0
Water to make 1 liter.	
Bleaching bath:	
Potassium ferricyanide	100.0
Potassium bromide	20.0
Disodium phosphate	10.0
Glacial acetic acid	4.0
Water to make 1 liter.	
Fixing bath:	
Sodium thiosulfate	200.0
Water to make 1 liter.	

The results are presented in Table 5.

TABLE 5

Sample	Addition/mole AgX	Sensitivity	Density
A	No addition	100	0.20
B	1.3 g. of Compound VII	150	0.21

EXAMPLE 4

An optical sensitizer for the red spectral region and a color coupler for a cyan image (1-hydroxy-2-naphthoic acid-2'-(methyl - n - octyldecylamino)-5'-sulfonic acid anilide) were added to a silver halide emulsion as in Example 3.

The other additions corresponded to those of Example 3.

The emulsion was divided in half and Part A was coated without an addition (standard); Part B received 1.2 g. of Compound XIII per mole of silver halide.

Processing was carried out as in Example 3.

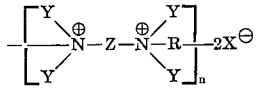
TABLE 6

Sample	Addition/mole of AgX	Sensitivity	Density
A	No addition	100	0.18
B	1.2 g. of Compound XIII	140	0.20

It can be seen from Examples 3 and 4 that the substances of the invention are also effective in emulsions containing color couplers. They increase the sensitivity without appreciably increasing the fog.

We claim:

1. A process for improving the sensitivity of a light-sensitive silver halide emulsion layer, comprising effecting the development of said emulsion layer after exposure thereof in the presence, as a chemical sensitizer in the emulsion layer, of a water-soluble quaternization product having the following general formula:



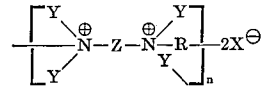
wherein Y is a radical selected from the group consisting of alkyl, phenylalkyl, hydroxyalkyl, alkoxyalkyl, acyloxyalkyl, aminoalkyl, alkylamino-alkyl and acylaminoalkyl, the alkyl group of said radical having up to 18 C atoms; R and Z are divalent organic radicals, at least one of the

radicals R and Z being a polyalkylene oxide group; $n=2-100$; and X is an anion.

2. A process according to claim 1, wherein said quaternization product has an average molecular weight of more than 2000.

3. A process according to claim 1, wherein R and Z stand for a polyethylene oxide bridge.

4. Light-sensitive material comprising at least one silver halide emulsion layer containing as a chemical sensitizer a quaternization product having the following general formula:



wherein Y is a radical selected from the group consisting of alkyl, phenylalkyl, hydroxyalkyl, alkoxyalkyl, acyloxyalkyl, aminoalkyl, alkylamino-alkyl, and acylaminoalkyl, the alkyl group of said radical having up to 18 C atoms; R and Z are divalent organic radicals, at least one of the radicals R and Z being a polyalkylene oxide group; $n=2-100$; and X is an anion.

5. Light-sensitive material according to claim 4, wherein said quaternization product has an average molecular weight of more than 2000.

6. Light-sensitive material according to claim 4, wherein R and Z stand for a polyethylene oxide bridge.

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NORMAN G. TORCHIN, Primary Examiner

A. T. SUROPICO, Assistant Examiner

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