PHOTOGRAPHIC SILVER HALIDE EMULSIONS WHICH INCLUDE HIGH EFFICIENCY SULFUR-CONTAINING SENSITIZERS

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12 Claims

ABSTRACT OF THE DISCLOSURE

Photographic light-sensitive emulsions are disclosed which include a sensitizing agent comprising the formula:

\[
\text{R}_1 \quad \text{N} \quad \text{C} \quad \text{A} \quad \text{C} \quad \text{N} \quad \text{R}_4
\]

wherein:
- \( A \) is a sulfur atom,
- each of \( R_1, R_2, R_3 \), and \( R_4 \) is hydrogen, alkyl, or aryl, or \( R_1 \) and \( R_2 \) and/or \( R_3 \) and \( R_4 \) together are the atoms necessary to close a heterocyclic ring, and
- \( n \) is zero or one.

The present invention relates to chemically sensitized, photographic, light-sensitive silver halide emulsions and to a photographic material comprising a light-sensitive layer coated from such emulsion.

It is known that photographic silver halide emulsions can be chemically sensitized by means of different kinds of compounds, which considerably enhance the sensitivity and sometimes the gradation too. The known chemical sensitizers can be divided into three main classes:

(a) Compounds comprising a labile sulphur atom, the so-called sulphur sensitizers, among which sodium thiosulphate and the thiourea compounds are best known;
(b) Reducing compounds such as tin (II) chloride and thiourea dioxide;
(c) Salts of noble metals such as gold, platinum or palladium salts.

It is also known that the light-sensitivity of silver halide emulsions, at least to some extent, results from the presence of sulphur compounds in the so-called "active gelatin."

Since the use of inert gelatin for the preparation of silver halide emulsions finds more and more acceptance in the photographic industry, the use of chemical sulphur sensitizers has become of increasing interest. The known sulphur sensitizers such as sodium thiosulphate and thiourea compound however are only usable in specific experimental conditions. They act only in rather narrow pH-ranges and at specific \( \text{pAg} \)-values of the emulsion. For instance, sodium thiouosulphate can be used as chemical sensitizers for washed silver bromide emulsions but only a slight increase in sensitivity is observed in the case of silver chloride emulsions and no increase at all in the case of silver iodide emulsions. Unwashed silver bromide emulsions too, i.e., emulsions with high \( \text{pAg} \)-value, can only be very difficultly sensitized with the known chemical sulphur sensitizers.

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

\[
\begin{align*}
\text{R}_1 & \quad \text{N} \\
\text{C} & \quad \text{A} \\
\text{C} & \quad \text{N} \\
\text{R}_4
\end{align*}
\]
The following examples illustrate the present invention.

**EXAMPLE 1**

A silver bromo-iodide emulsion (3 mole percent of iodide) prepared with inert gelatin and having an average grain size of 0.12 micron, a pAg of 7.5 and a pH of 6.5 is divided into three equal parts (samples A, B, and C). The sulphur sensitizers listed in Table I are added to samples B and C in the given concentrations. The emulsions are then ripened at 45°C for 3 hours whereupon they are coated on a cellulose tricetate support. The test-strips obtained are developed after exposure in a hydroquinone-p-monomethyl-aminophenol hemisulphate developer, fixed and rinsed whereupon the speed is measured. In Table I the relative speeds are listed.

**TABLE I**

<table>
<thead>
<tr>
<th>Sulphur sensitizer</th>
<th>Concentration per mole of silver halide</th>
<th>Rel. speed</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td></td>
<td>100</td>
</tr>
<tr>
<td>B</td>
<td>Compound 2</td>
<td>100</td>
</tr>
<tr>
<td>C</td>
<td>Compound 3</td>
<td>100</td>
</tr>
</tbody>
</table>

**EXAMPLE 2**

A gold thiocyanate solution is added in an amount equivalent to 5 mg. of gold per mole of silver halide to a same emulsion as described in Example 1 just before dividing the emulsion in samples A, B, and C and before the addition of compounds 2 and 3 in the given concentration to samples B and C. The three samples are coated and further treated as described in Example 1. The materials according to the present invention show a sensitivity that is 3 times as high as that of the light-sensitive material containing only gold rhodanide and no chemical sensitizer according to the present invention.

**EXAMPLE 3**

An all-silver iodide emulsion prepared with inert gelatin and having a pAg of 9 and a pH of 6.5 is divided into four equal parts A, B, C, and D. To each part is added the chemical sensitizer listed in Table II hereinafter in the concentration given. After having been ripened for 1 hour at 50°C, the four emulsions are coated on a cellulose tricetate support. The light-sensitive materials obtained are exposed and further treated as described in Example 1. The relative speeds are given in Table II.

**TABLE II**

<table>
<thead>
<tr>
<th>Sulphur sensitizer</th>
<th>Concentration per mole of silver halide</th>
<th>Rel. speed</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td></td>
<td>100</td>
</tr>
<tr>
<td>B</td>
<td>Sodium thiosulphate</td>
<td>100</td>
</tr>
<tr>
<td>C</td>
<td>Compound 1</td>
<td>200</td>
</tr>
<tr>
<td>D</td>
<td>Compound 2</td>
<td>120</td>
</tr>
</tbody>
</table>

**EXAMPLE 4**

An all-silver chloride emulsion prepared with inert gelatin and having an average grain size of 0.12 micron, a pAg of 7.5 and a pH of 6.5 is divided into three equal parts A, B, and C. The compounds listed in Table III are added to each emulsion part in the concentration given. After an optimum ripening period of 1½ hours at 50°C, the three emulsions are coated on a cellulose tricetate support whereupon the materials obtained are further treated as described in Example 1. The relative speeds of the materials are listed in Table III.

**TABLE III**

<table>
<thead>
<tr>
<th>Sulphur sensitizer</th>
<th>Concentration per mole of silver halide</th>
<th>Rel. speed</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Sodium thiosulphate</td>
<td>100</td>
</tr>
<tr>
<td>B</td>
<td>Compound 1</td>
<td>200</td>
</tr>
<tr>
<td>C</td>
<td>Compound 10</td>
<td>300</td>
</tr>
</tbody>
</table>

**EXAMPLE 5**

To the same kind of emulsion as described in Example 4 a gold thiocyanate solution is added, in an amount
equivalent to 7 mg. of gold per mole of silver halide, before dividing the emulsion into samples, and adding a chemical sensitizer according to the invention. The emulsion is divided into two equal parts and to one part 0.7 x 10^{-4} mole of compound 10 per mole of silver chloride is added. The emulsions are coated and further treated as described in Example 4. The speed of the light-sensitive material comprising compound 10 is 3 times as high as that of the other material.

**EXAMPLE 6**

An ammoniacal silver bromo iodide emulsion (3 mole percent of iodide) which has been prepared with inert gelatin, and which has not been washed as was the case with the emulsions of the preceding examples, is divided immediately after its preparation into 3 equal parts (samples A, B and C). The sulphur sensitisers listed in Table IV are added to samples B and C in the given concentrations. After having been kept for 30 min. at 35°C, the three samples are coated onto a cellulose triacetate support and further treated as in Example 1. The relative speeds of the three materials are listed in Table IV.

<table>
<thead>
<tr>
<th>Sulphur sensitizer</th>
<th>Concentration per mole of silver halide</th>
<th>Rel. speed</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Sodium thiomaldehyde 5x10^{-4} mole</td>
<td>100</td>
</tr>
<tr>
<td>B</td>
<td>Composed of 5x10^{-4} mole</td>
<td>100</td>
</tr>
<tr>
<td>C</td>
<td></td>
<td>150</td>
</tr>
</tbody>
</table>

**EXAMPLE 7**

240 cc. of a 3M aqueous silver nitrate solution and 240 cc. of a 3M aqueous potassium bromide solution are simultaneously and slowly added at 35°C to a solution of 50 g. of gelatin in 500 cc. of water (emulsion A). A second emulsion is prepared in the same way with the only difference that the aqueous gelatin solution to which the aqueous silver nitrate and the potassium bromide solutions are added also comprises 9 mg. of compound 2 (emulsion B).

Emulsions A and B are physically ripened by keeping them for 60 min. at 45°C. Electron micrographs (magnification 10,000 x) are taken from the ripened liquid emulsions. In both cases, these micrographs shows a dispersion of silver bromide grains ranging for the greater part from about 0.05 to about 0.1μ. Emulsion A, however, also contains a considerable number of grains ranging from about 0.5 to about 1.0μ whereas emulsion B only contains some grains which are of larger size than 0.1μ. From the results obtained it clearly appears that the presence of a chemical sensitizer according to the present invention during the precipitation of the silver halide and the physical ripening of the emulsion obtained prevents in a very efficient way the formation of large silver halide grains.

We claim:

1. Photographic light-sensitive silver halide emulsion containing as a sensitizer at least one compound corresponding to the following general formula:

   \[
   R_1=N-C=-A\quad-C-N=R_4
   \]

   wherein:
   A is a sulphur atom, each of R_1, R_2, R_3 and R_4 is hydrogen, alkyl, or aryl, or R_1 and R_2 and/or R_3 and R_4 together are the atoms necessary to close a heterocyclic ring, and
   n is zero or one.

2. Photographic light-sensitive emulsion according to claim 1, wherein the silver halide emulsion includes a protective colloid consisting substantially of inert gelatin.

3. Photographic light-sensitive emulsion according to claim 1, wherein the emulsion is an unwashed silver halide emulsion.

4. Photographic light-sensitive emulsion according to claim 1, wherein the silver halide of the emulsion consists substantially of silver chloride.

5. Photographic light-sensitive emulsion according to claim 1, wherein the silver halide of the emulsion consists substantially of silver iodide.

6. Photographic light-sensitive emulsion according to claim 1, wherein the emulsion is a fine-grain emulsion.

7. The photographic light-sensitive emulsion of claim 1 wherein the emulsion includes a polyeoxyalkylene derivative having a molecular weight higher than 500.

8. Photographic light-sensitive emulsion according to claim 1, wherein the emulsion consists of a nonium compound.

9. Photographic light-sensitive emulsion according to claim 1, wherein the emulsion includes a gold salt.

10. Photographic light-sensitive emulsion according to claim 1, wherein the sensitizer is present in an amount of from 1 to 200 mg. per mole of silver halide.

11. Photographic light-sensitive emulsion according to claim 1, wherein the emulsion includes a gold salt.

12. Photographic light-sensitive emulsion according to claim 11, wherein said gold salt is gold thioacetate.

**References Cited**

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NORMAN G. TORCHIN, Primary Examiner
A. T. SUROPICO, Assistant Examiner

U.S. Cl. X.R.

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