METHOD OF DESENSITIZING LIGHT-SENSITIVE SILVER HALIDE PHOTOGRAPHIC MATERIALS WITH CYCLOHEPTIMIDAZOLE DERIVATIVES

13 Claims, No Drawings

wherein R₁ is hydrogen, lower alkyl, halogen, cyano or dialkyl amino and R₂ is aryl or pyridinium which may or may not be substituted.
3,615,607

METHOD OF DESENSITIZING LIGHT-SENSITIVE SILVER HALIDE PHOTOGRAPHIC MATERIALS WITH CYCLOHEPTIMIDAZOLE DERIVATIVES

CROSS-REFERENCE TO RELATED APPLICATION

This application is a division of copending application Ser. No. 622,475; filed Mar. 13, 1967 and claiming a priority of Mar. 19, 1966 based on an application filed in Japan.

DETAILED DESCRIPTION OF THE INVENTION

This invention relates to the desensitization of light-sensitive silver halide photographic materials. The desensitizer which is used in the method of the invention has the chemical structure represented by the general formula (1) shown below. It is the principal object of the present invention to provide for desensitization without any staining or coloration of photographic pictures and in accordance therewith, there is provided a method in which use is made of desensitizers which exert no adverse influence on the contrast of photographed images.

Therefore, a number of compounds have been known to be useful as desensitizers for light-sensitive silver halide photographic materials, which compounds include, for example, phenoisafarine, malachite green, pinacryptol yellow, pinacyryptol green, etc. These known desensitizers suffer from several disadvantages and are not satisfactory in actual use. For instance, some of these desensitizers will stain or color the photographic picture or will impair the photographic properties of the resulting image, because they are themselves inherently colored substances. More specifically, phenoisafarine which is a substance having red color usually causes reddish coloration of the photographic materials, sometimes with a decrease in contrast of the photographed images. Malachite green and pinacryptol green, both of which are green compounds, will decrease the whiteness of the background of photographic pictures. Furthermore, pinacryptol green sometimes has an adverse effect on the stability of a fogged emulsion. Pinacryptol yellow, which is generally preferred among the known desensitizers because it causes no problem in the contrast of photographic images, will nevertheless cause yellowish coloration which decreases the whiteness of the surface of photographic materials. Moreover, it has a serious disadvantage which is its instability in developing solutions. Thus, all the known desensitizers are not satisfactory because of their undesirable influence on the photographic properties of the resulting images.

In accordance with the present invention, there is provided a new desensitizing method which uses a desensitizing compound having the following chemical structure:

\[
\text{R}_1 N \text{C} = \text{N} \text{R}_2
\]

where in \( \text{R}_1 \) is hydrogen, lower alkyl, halogen, cyano or dimethylamino and \( \text{R}_2 \) is aryl or pyridinium group which may or may not be substituted.

The compounds defined above are available at relatively cheap cost. Almost all of these are colorless substances, and the other few are substances which have very slight color insufficient to cause coloration. The compounds all meet the following photographic requirements:

1. They should have the capability of decreasing photographic sensitivity;
2. They should not cause fogging or decrease in contrast;
3. They should not affect fogged silver halide crystals;
4. They should not contaminate binders (e.g., gelatine) or supports; and
5. They should be soluble in water. It is, of course possible to use the compounds in a developing solution.
These compounds can be used as desensitizers for photographic purposes in the same manner as the known desensitizers for light-sensitive silver halide photographic materials. For example, in accordance with the invention, an exposed high-speed photographic film can be pretreated with an aqueous solution of the desensitizer of the present invention so that the film may be developed under relatively bright conditions which enables one to conduct the development with visual inspection of the progress of development. Alternatively, the desensitizer can be added to the developing solution to be used for photographic development, whereby an exposed photographic film can be treated with said solution under relatively bright conditions because of its decreased sensitivity. Incorporation of the desensitizer into a light-sensitive silver halide photographic emulsion having fogged silver halide crystals can provide one with a direct-positive, light-sensitive material which directly yields a positive image through the Herschel effect or solarization.

If the desensitizer is used as a pretreating bath for imagewise exposed, light-sensitive silver halide photographic materials, it is conveniently prepared in the form of an aqueous solution at a concentration of 0.01–0.03 percent. After dipping in this solution for several minutes, the photographic material can be treated with a conventional developing solution under relatively bright safelight. If the desensitizer is used in a developing solution, it should be in amount of 0.003 to 0.02 percent. By use of the desensitizer in accordance with the invention, developing procedures can be performed under such bright safelight which allows one to make visual inspection of the result of the developed images. Of course, there is no problem of coloration of the developed images or of any damage to the contrast of the images.

For the preparation of a direct-positive light-sensitive photographic material, the desensitizer is used according to the invention in the amount of 0.005–1 g. per 100 g. of silver nitrate, the amount of which is calculated from the silver halide content of the light-sensitive emulsion used. The appropriate amount of the desensitizer is dissolved in water or lower alcohol such as methanol or ethanol or a mixture thereof and the resulting solution is added to the light-sensitive emulsion containing fogged silver halide crystals. Usually it is preferred to combine the desensitizer solution with the fogged emulsion just before the coating of the resulting mixture on a support, but this is not critical. The thus prepared direct-positive light-sensitive material exhibits a much improved Herschel effect, by which an image free of any coloration and with high contrast is obtained.

The following examples describe certain embodiments of the invention, but are not be construed as limiting the scope thereof.

**EXAMPLE 1**

2-(m-nitrophenyl)-cycloheptimidazole was prepared as an 0.02 percent aqueous solution, into which a commercially available, high-speed panchromatic photographic film was dipped for 2 minutes, thereby to have its original sensitivity decreased to 1/100. Thus, the treated film could be subjected to development under relatively bright safelight. After the development, the films did not show any coloration or contamination.

Alternatively, 0.1 g. of 2-(m-nitrophenyl)-cycloheptimidazole was added to a developing solution of the following formulation:

- Monomethyl-p-aminophenol sulfate: 2.0 g.
- Sodium sulfite (anhydrous): 8.0 g.
- Hydroquinone: 4.0 g.
- Borax: 4.0 g.
- Potassium bromide: 0.5 g.
- Distilled water to make up 1000 ml.

By using the resulting mixture, a commercially available high-speed panchromatic photographic film was treated. The procedures can be effected under relatively bright safelight conditions, without causing any coloration or contamination.
EXAMPLE 2

One kilogram of a pure silver chloride emulsion containing the equivalent of 40 g. of silver nitrate was buffered to a pH of 8.0 by the addition of 30 ml. of aqueous solution of 6 percent sodium carbonate. Then, the emulsion was mixed with 7 ml. of 3 percent formalin and heated at 50°C. for 60 minutes. The thus fogged emulsion was buffered to pH 6.0 by the addition of an aqueous solution of 10 percent citric acid. The emulsion was divided into 10 portions, each of which was mixed with the compound indicated in Table 1. The respective portions were coated on photographic papers and then dried. The thus prepared direct-positive, light-sensitive photographic sheets were subjected to stepwise exposure to light through a yellow filter which passes light of a wavelength longer than 450 μ and then treated with a D-72 type developer. The sensitometric results obtained are set forth below:

Table 1

<table>
<thead>
<tr>
<th>Compound added</th>
<th>Amount added</th>
<th>Reversal photographic speed</th>
<th>Photographic gamma</th>
<th>Minimum reversal density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pinacryptol yellow 1</td>
<td>10 mg.</td>
<td>100</td>
<td>3.50</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Compds. (1)</td>
<td>10 mg.</td>
<td>92</td>
<td>3.00</td>
<td>0.04</td>
</tr>
<tr>
<td>Compds. (2)</td>
<td>10 mg.</td>
<td>100</td>
<td>3.53</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Compds. (3)</td>
<td>10 mg.</td>
<td>110</td>
<td>3.60</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Compds. (5)</td>
<td>10 mg.</td>
<td>108</td>
<td>3.59</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Compds. (9)</td>
<td>10 mg.</td>
<td>114</td>
<td>3.65</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Compds. (10)</td>
<td>10 mg.</td>
<td>110</td>
<td>3.62</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Compds. (11)</td>
<td>10 mg.</td>
<td>105</td>
<td>3.55</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Compds. (16)</td>
<td>10 mg.</td>
<td>108</td>
<td>3.58</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>

1) Pinacryptol yellow and phenosaframine were used as control desensitizers.

2) This is expressed as a specific value as compared with the reversal photographic speed of the pinacryptol yellow-loaded photographic sheet, which is rated as 100.

As is apparent from Table 1, the sheets in which the desensitizers of this invention were used were excellent in photographic speed and contrast, whereas the control sheets loaded with pinacryptol yellow and phenosaframine suffered respectively from yellowish or reddish coloration.

EXAMPLE 3

One kilogram of a pure silver chloroiodide emulsion containing the equivalent of 40 g. of silver nitrate was buffered to pH 7.5 by the addition of 25 ml. of 5 percent aqueous sodium carbonate solution. Then, the emulsion was mixed with 10 ml. of 3 percent formalin and heated at 55°C. for 40 minutes. The thus fogged emulsion was buffered to pH 6.0 by the addition of an aqueous solution of 10 percent citric acid. The emulsion was divided into 10 portions, each of which was mixed with the compound indicated in Table 2. The respective portions were coated on photographic papers and then dried. The thus prepared 10 direct-positive, light-sensitive photographic sheets were subjected to stepwise exposure to white light and then treated with a developing solution. The sensitometric results obtained are set forth below:

Table 2

<table>
<thead>
<tr>
<th>Compound added</th>
<th>Amount added</th>
<th>Reversal photographic speed</th>
<th>Photographic gamma</th>
<th>Reversal minimum density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pinacryptol yellow</td>
<td>20 mg.</td>
<td>925</td>
<td>3.58</td>
<td>0.06</td>
</tr>
<tr>
<td>Compds. (1)</td>
<td>20 mg.</td>
<td>730</td>
<td>2.82</td>
<td>0.10</td>
</tr>
<tr>
<td>Compds. (2)</td>
<td>20 mg.</td>
<td>910</td>
<td>3.57</td>
<td>0.03</td>
</tr>
<tr>
<td>Compds. (3)</td>
<td>20 mg.</td>
<td>1,020</td>
<td>3.70</td>
<td>0.02</td>
</tr>
<tr>
<td>Compds. (5)</td>
<td>20 mg.</td>
<td>1,100</td>
<td>3.75</td>
<td>0.01</td>
</tr>
<tr>
<td>Compds. (9)</td>
<td>20 mg.</td>
<td>1,180</td>
<td>3.75</td>
<td>0.01</td>
</tr>
<tr>
<td>Compds. (10)</td>
<td>20 mg.</td>
<td>1,120</td>
<td>3.74</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Compds. (11)</td>
<td>20 mg.</td>
<td>1,050</td>
<td>3.62</td>
<td>0.02</td>
</tr>
<tr>
<td>Compds. (16)</td>
<td>20 mg.</td>
<td>1,090</td>
<td>3.69</td>
<td>0.01</td>
</tr>
</tbody>
</table>

As is apparent from Table 2, the sheets in which the desensitizers of the invention were used were better in reversal minimum density and contrast, while the control sheets suffered from coloration of their surfaces.

What is claimed is:

1. A method comprising treating light-sensitive silver halide photographic materials with a desensitizing amount of a compound having the chemical formula

$$\text{R}_1\text{N} - \text{N} - \text{R}_2$$

wherein \( \text{R}_1 \) is hydrogen, lower alkyl, halogen, cyano or a 4-, 6- or 7-positioned dimethylamino and \( \text{R}_2 \) is phenyl, phenyl substituted by nitro, bromo, amino, dimethylamino, methoxy or methyl; or pyridinium or pyridinium substituted by carbamoyl or methoxy carbonyl.

2. A method as claimed in claim 1, wherein \( \text{R}_1 \) is hydrogen and \( \text{R}_2 \) is phenyl.

3. A method as claimed in claim 1, wherein \( \text{R}_1 \) is 4-positioned bromine and \( \text{R}_2 \) is phenyl.

4. A method as claimed in claim 1, wherein \( \text{R}_1 \) is hydrogen and \( \text{R}_2 \) is m-nitrophenyl.

5. A method as claimed in claim 1, wherein \( \text{R}_1 \) is hydrogen and \( \text{R}_2 \) is o-nitrophenyl.

6. A method as claimed in claim 1, wherein \( \text{R}_1 \) is hydrogen and \( \text{R}_2 \) is p-anisyl.

7. A method as claimed in claim 1, wherein \( \text{R}_1 \) is hydrogen and \( \text{R}_2 \) is pyridinium chloride.

8. A method as claimed in claim 1, wherein \( \text{R}_1 \) is hydrogen and \( \text{R}_2 \) is 3-carbamoylpyridinium chloride.

9. A method as claimed in claim 1, wherein \( \text{R}_1 \) is hydrogen and \( \text{R}_2 \) is 3-methoxycarbonylpyridinium chloride.

10. A method as claimed in claim 1, wherein \( \text{R}_1 \) is hydrogen and \( \text{R}_2 \) is 3-methoxy carbonylpyridinium chloride.

11. A method as claimed in claim 1, wherein \( \text{R}_1 \) is 6-positioned dimethylamino and \( \text{R}_2 \) is phenyl.

12. A method as claimed in claim 1, wherein \( \text{R}_1 \) is 6-positioned bromine and \( \text{R}_2 \) is phenyl.

13. A method as claimed in claim 1, wherein \( \text{R}_1 \) is hydrogen and \( \text{R}_2 \) is p-nitrophenyl.