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# DIRECT POSITIVE SILVER HALIDE PHOTOGRAPHIC MATERIALS

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## ABSTRACT OF THE DISCLOSURE

A direct positive photographic element comprising a fogged silver halide emulsion layer and an adjacent gelatin layer, at least one of said layers containing as a desensitizer 3-nitrophenyl thiazoline-2-thiones.

The present invention relates to photography and particularly to an improved direct positive photographic material.

It is known that, if a photographic silver halide emulsion, which has been exposed to blue light, is subsequently exposed to long-wave radiation before it is developed, the effect of the original exposure is partly destroyed. This is known under the name of Herschel-effect and may be used for obtaining a reversed image.

There has been already described a method of producing a direct positive emulsion, in which there is incorporated in a silver halide emulsion a portion of a desensitizing compound in order to enhance the Herschel effect and then the image is fogged by light or chemical means. When thus prepared emulsion is exposed to red light followed by developing, a positive image is directly produced.

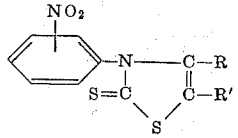
In fact, however, suitable desensitizing compounds for the above process are quite rare. As such desensitizing compounds there have been proposed compounds each having a nitro group attached to the benzene nucleus thereof, such as, benzthiazole, quinoline, indoline, benztriazole, rhodanine compounds and their quaternary salts.

Phenosafranin and Pinakryptol Yellow are well-known desensitizing compounds in the art, but there is a practical limit to the advantages that can be obtained by the addition of such desensitizing compounds without accompanying deleterious effect, such as, uncontrollable coloring of the photographic material and depressing their photographic gradation.

It is an object of the invention to provide an improved positive photographic material.

Another object of this invention is to provide new desensitizing compounds that can enhance the Herschel effect and give no coloring on the finished paper or film.

According to the present invention there is provided a direct positive photographic emulsion that has been fogged by light or chemical means, said photographic material containing a desensitizing compound of the general formula

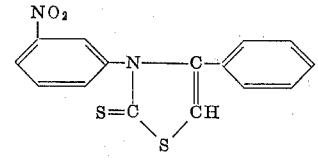


wherein R represents hydrogen, a lower alkyl group, or a phenyl group and R′ represents hydrogen, a lower alkyl group, or a carboalkoxy group.

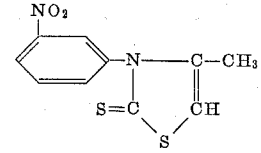
Examples of the desensitizing compounds shown by the above formula are as follows, although the desensitizing compounds used in this invention are not by any means limited to only these compounds:



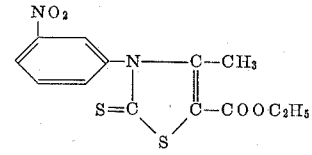
*Compound 1.—3-(3-nitrophenyl)-4-phenylthiazoline-2-thione*



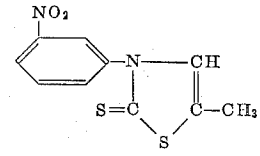
*Compound 2.—4-methyl-3-(3-nitrophenyl)thiazoline-2-thione*



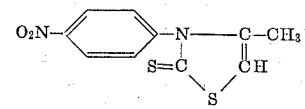
*Compound 3.—4-methyl-3-(3-nitrophenyl)-5-ethylcarboxy-thiazoline-2-thione*



*Compound 4.—5-methyl-3-(3-nitrophenyl)thiazoline-2-thione*



*Compound 5.—4-methyl-3-(4-nitrophenyl)thiazoline 2-thione*



These compounds may be incorporated in silver chloride, silver chloro-bomide or silver bromo-iodide emulsions. The optimum amount of the desensitizing compound is between 0.04 g. and 0.4 g. per kilogram of the emulsion. In general, the same amounts per square meter are used.

The followings illustrate the examples for synthesizing several desensitizers mentioned above.

*Compound 1.—3-(3-nitrophenyl)-4-phenylthiazoline-2-thione*

31.5 g. (0.1 mole) of a triethylammonium salt of 3-nitroanilinedithiocarbamic acid was suspended in alcohol, 19.9 g. (0.1 mole) of ω-bronacetophenone was then added in the suspension, and the mixture was, after acidified with sulfuric acid, refluxed for 30 minutes. After cooling, the deposited crystals were separated by filtration. By recrystallization, 8 g. of yellow fine crystals having a melting point of 192–193° C. were obtained.

*Compound 2.—4-methyl-3-(nitrophenyl)thiazoline-2-thione*

31.5 g. (0.1 mole) of a triethylammonium salt of 3-nitroanilinedithiocarbamic acid was suspended in alcohol, 9.3 g. (0.1 mole) of chloroacetone was added dropwise in suspension, and the mixture was, after acidified with sulfuric acid, refluxed for 30 minutes. After cooling, the deposited crystals were separated by filtration, rinsed with water and dissolved into alcohol followed by recrystallization. By the treatment, 10 g. of yellow crystals having a melting point of 159–160° C. were obtained.

*Compound 5.—4-methyl-3-(4-nitrophenyl)thiazoline-2-thione*

The above compound was synthesized in the process shown in "Liebig Annalen," vol. 647, page 72 (1961).

A mixture of 10.0 g. (0.06 mole) of 4-nitro-phenylisocyanate and 6.0 g. (0.07 mole) of mercaptoacetone was heated for 3 hours to 120–130° C. After cooling, the product was dissolved with 55 ml. of ethyl acetate under heating and filtered. By cooling the solution, yellow crystals were deposited, which were separated by filtration and recrystallized in ethyl acetate. The melting point of thus obtained crystal was 179–181° C.

The following examples will serve to illustrate the embodiments of this invention.

## EXAMPLE 1

A silver chloro-bromide emulsion (50 g. $AgNO_3$/1 kg. emulsion) containing 30 mole percent of silver bromide was, after washing ripened for about 40 minutes at 50° C. After adjusting the pH of the emulsion to about 8.0, 15 ml. of a 1% aqueous hydroxylamine solution was added and the system was kept at the same temperature for 10 minutes. Thereafter, the pH of the system was adjusted to 6.0.

Then, 100 ml. of a 0.1% methanol solution of Compound 1, 20 ml. of a 5% aqueous chrome alum solution, and 10 ml. of a 5% aqueous saponin solution were successively added in 1 kg. of the emulsion. The emulsion was coated on a paper and dried by conventional means.

Thus prepared photographic sensitive material was exposed for 10 seconds from a distance of 10 cm. with a 1 kw. mercury lamp to an image through a yellow filter (e.g., Kodagraph Sheeting Yellow). The photographic material was then developed for 60 seconds at 20° C. in D–72 developer, fixed and dried to give a direct positive image having a good quality.

## EXAMPLE 2

A silver chloride emulsion (40 g. $AgNO_3$/1 kg. emulsion) was ripened at 50° C. for 10 minutes.

After adjusting the pH of the emulsion to about 8.0, 20 ml. of a 1% hydroxylamine solution was added and the system was kept at the same temperature for 50 minutes to give sufficient chemical fog, and then the pH of the emulsion was adjusted to 5.5.

The emulsion was cooled to set and washed to remove excess salts. 120 ml. of a 0.1% methanol solution of Compound 2, 80 ml. of a 25% ethanol solution of hydroquinone, 3 ml. of a 2% benztriazole solution, 10 ml. of a 5% aqueous saponin solution, 10 ml. of a 5% aqueous chrome alum solution, and 10 ml. of a 40% formalin were added to 1 kg. of the washed emulsion successively. The emulsion was coated on a paper and dried. The coating was exposed in the similar manner in Example 1, and processed through a rapid processing means which comprised a high alkaline activator and a stabilizing solution. A positive image was obtained in about 10 minutes.

In this example, almost same direct positive image were obtained by using Pinakryptol yellow instead of Compound 2, but the whiteness in the reversed portion in this case was inferior to the case of using Compound 2.

## EXAMPLE 3

One kg. of a washed silver chloro-iodide emulsion (1 mole percent silver iodide) containing the equivalent of 40 g. silver nitrate was ripened at 55° C. for about 30 minutes and the pH was adjusted to 8.0.

Two ml. of an aqueous solution of formaldehyde (40%) was added in the emulsion, which was then kept at the same temperature for 10 minutes to give sufficient chemical fog.

The pH was adjusted to 6.0 and 150 ml. of a 0.1% solution in methanol of Compound 3, 10 ml. of a 5% aqueous chrome alum solution and 10 ml. of a 5% aqueous saponin solution were added with stirring. The emulsion was then coated on a film support having a backing of anti-halation layer and dried.

This chemically fogged emulsion was exposed to an image as in Example 1 and processed.



## EXAMPLE 4

150 ml. of a 0.1 methanol solution of Compound 4 was added into 1 kg. of a silver chloride emulsion containing the equivalent of 30 g. of silver nitrate and 20 ml. of a 5% aqueous chrome alum solution, and 10 ml. of a 5% aqueous saponin solution were added successively.

Then the emulsion was coated on a paper support and exposed to white light sufficient to give a density of at least 1.5 when developed in D–72 developer (1:2). This pre-exposed material was exposed to an image through a yellow filter as in Example 1, developed, fixed, washed and dried.

A direct positive image having better whiteness and higher maximum density than those in the case of using Pinakryptol yellow was obtained.

## EXAMPLE 5

An orthochromatic ammonia type silver halide emulsion (predominately silver bromide with small traces of silver iodide) containing 40 g. silver nitrate per kilogram of liquid emulsion was prepared in conventional manner and added with suitable addition agents.

The emulsion was coated on a cellulose acetate film base having a backing of anti-halation layer in 7 microns in the dried state and set on cooling. Thereafter, a 2% gelatin solution containing 80 ml. of a 0.1% methanol solution of Compound 5 per 1 liter of the solution and suitable amount of glycerin, chrome alum and saponin, was coated over the previously formed coating and dried.

The emulsion layer so prepared was pre-exposed as in Example 4 and exposed for 10 seconds from a distance of 1 m. with a 500 w. incandescent lamp to an image through a red filter which did not transmit any light below 600 millimicrons, and processed in similar manner as in Example 1.

A direct positive image was obtained with a high quality. Yellow coloring of the material was considerably less than that in case of using Pinakryptol yellow instead of Compound 5.

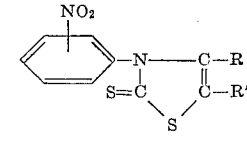
## EXAMPLE 6

A photographic emulsion prepared as described in Example 5 was added with 120 ml. of a 0.1% methanol solution of Compound 1 per kilogram of the emulsion, and coated on a suitable film support. Then, it is allowed to set and overcoated with a 2% gelatin solution containing 30 ml. of a methanol solution of Compound 3 per liter of the solution.

The coating was exposed for the same period and processed as in Example 5. A direct positive image was obtained on an improved clear base.

What is claimed is:

**1.** A direct positive photographic element comprising a fogged silver halide emulsion layer and an adjacent gelatin layer, at least one of said layers containing as a desensitizer a compound of the following general formula




wherein R is a member selected from the class consisting of hydrogen, a lower alkyl group, and a phenyl group and R' is a member selected from the class consisting of hydrogen, a lower alkyl group, and a carboalkoxy group.

**2.** The silver halide photographic material according to claim **1** wherein said layer containing the compound is a photographic fogged silver halide emulsion layer and

the content of the compound being about 0.04 to about 0.4 g. per 1 kg. of said silver halide emulsion.

3. The silver halide photographic material according to claim 1 wherein said layer containing the compound is a gelatin layer adjacent the photographic emulsion layer.

4. The silver halide photographic material according to claim 1 wherein said compound is 3-(3-nitrophenyl)-4-phenylthiazoline-2-thione.

5. The silver halide photographic material according to claim 1 wherein said compound is 4-methyl-3-(3-nitrophenyl)thiazoline-2-thione.

6. The silver halide photographic material according to claim 1 wherein said compound is 4-methyl-3-(3-nitrophenyl)-5-ethylcarboxythiazoline-2-thione.



7. The silver halide photographic material according to claim 1 wherein said compound is 5-methyl-3-(3-nitrophenyl)thiazoline-2-thione.

8. The silver halide photographic material according to claim 1 wherein said compound is 4-methyl-3-(4-nitrophenyl)thiazoline-2-thione.

**References Cited**

UNITED STATES PATENTS

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| 2,541,472 | 2/1951 | Kendall et al. | 96—101 |
| 2,901,351 | 8/1959 | Van Ree et al. | 96—101 |


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