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3,672,902

**PHOTOGRAPHIC SILVER HALIDE EMULSION  
WITH IMPROVED SAFE-LIGHT SENSITIVITY**

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8 Claims

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**SUMMARY OF THE INVENTION**

This invention provides a highly effective sensitizer combination which markedly increases the sensitivity of the emulsion in the blue region and at the same time desensitizes the longer-wave region, that is, reduces the sensitivity in the red and, above all, in the green region. The goal is to produce highly sensitive emulsions that can be processed with high-intensity, green safe lights without deleterious effects. According to the invention, this problem is solved by adding a diphenyldisulfidedicarboxylic acid, a polyhydroxy-spiro-bis-indane, and a quantity of metol or 3-pyrazolidone insufficient for complete development, to the light-sensitive silver halide emulsion or to a gelatin-containing layer in contact with it. This combination considerably increases the sensitivity with low fog values and, in fact, selectively in the blue region of the spectrum, whereas, a lowering of the sensitivity is effected in the longer-wave spectral region, especially in the green region.

From French Pat. 1,395,324, it is known that diphenyldisulfidedicarboxylic acids can be used as stabilizers for photographic materials. The use of polyhydroxy-spiro-bis-indanes as tanning developers is known from Belgian Pat. 699,429. Numerous other publications have taught the introduction of developers, such as p-amino-phenols and 3-pyrazolidones, into photographic layers. These materials alone do not yield the effect described above. A combination of the compounds selectively increase the sensitivity in the blue region of the spectrum and lower the sensitivity in the green and red regions. This surprising fact and synergistic effect could not have been predicted from knowledge of the mode of action of the individual components. A considerable and surprising advance is achieved by their synergistic effect.

**DESCRIPTION OF THE PREFERRED  
EMBODIMENT**

To carry out the process, diphenyldisulfidedicarboxylic acids, especially diphenyldisulfide-2,2'-dicarboxylic acid, already mentioned in French Pat. 1,395,324, can be used. An especially suitable polyhydroxy-spiro-bis-indane compound is 3,3,3',3'-tetramethyl-4,5,4',5'-tetrahydroxy-spiro-bis-indane. However, the other compounds mentioned in the Belgian Pat. 699,429 also can be used. A procedure for preparing compounds of this type, according to information in the Belgian patent, is described in J. Chem. Soc. 1934, pages 1678-1681. 3-pyrazolidone developers are known in large numbers, for example, from the British patents 679,677, 679,678, and 767,704. The best-known compound of this group is 1-phenyl-3-pyrazolidone, which is obtainable in the market under the name "Phenidone." The compounds of the invention can be added directly to the light-sensitive silver halide emulsion and/or they can be introduced into a gelatin-containing intermediate layer located directly in contact with the emulsion. Accordingly, a part of the combination can be located in the light-sensitive layer and another in the light-insensitive secondary layer.

The compounds are added to the photographic films according to known procedures in a quantity usable for the purpose mentioned. The optimum quantities to be used in a particular case can be determined easily by those skilled in the art and generally amount to about 0.015-0.120 g. of the diphenyldisulfidedicarboxylic acid, 0.5-1.50 g. of a polyhydroxy-spiro-bis-indane compound, 0.01-0.10 g. of p-aminophenol, and 0.05-1.0 g. of 2-phenylpyrazolidone developer per mole of silver halide present in the emulsion. Preferably, the addition takes place after the chemical ripening and before coating the emulsions. The sensitizer combination of the invention is suitable for optically unsensitized silver halide emulsions, preferably for bromide-iodide emulsions such as those

**ABSTRACT OF THE DISCLOSURE**

Light-sensitive silver halide emulsions containing mixtures of a diphenyldisulfide carboxylic acid, a polyhydroxy-spiro-bis-indane, a developing agent and a poly-(alkylene oxide) compound. The emulsions have improved light-sensitivity with reduced sensitivity to safe-light illumination.

**BACKGROUND OF THE INVENTION**

This invention relates to photographic silver halide emulsions that contain combinations of sensitizers having a selective action that increase sensitivity.

It is known that the sensitivity of photographic silver halide emulsions can be increased through the addition of chemical sensitizers. Besides gold and sulfur compounds, poly(ethylene glycols), especially those with a molecular weight above 1500, have proven to be very useful agents for increasing the sensitivity. In addition, it is also known that chemical sensitizers in combination with suitable stabilizers and, if desired, still other compounds can also be used. With such combinations, considerable increases in the sensitivity are reported without increasing the fog to an objectionable degree. Such combinations are described, for example, in the German patent specifications 1,155,327 and 1,163,672.

In practical use, it has been found that the sensitivity-increasing action of such combinations is not selective only in the blue region of the spectrum, but that marked sensitivity of the emulsion also occurs in the red and, above all, in the green region of the spectrum. This secondary action is more pronounced when more effective sensitivity-increasing combinations are used. This additional increase in sensitivity in the longer-wave region is very detrimental and undesirable. Silver halide emulsions for radiographic purposes are used in combination with intensifying screens and are sensitive mainly to the blue light of the intensifying screen and in practice are usually processed with red or green safe lights. If now by chemical sensitization not only the sensitivity in the blue region is increased, but the sensitivity in the longer-wave region also is increased, then the photographic emulsion will not possess adequate resistance toward the safe light used in the dark room. This shortcoming is especially pronounced when green safe lights, such as the mercury high-pressure lamps with a line spectrum at 546 m $\mu$  and 579 m $\mu$ , are used in the dark room. The light radiated by these lamps is agreeably bright to the eye, because its maximum radiation is located in a physiologically favorable region of eye sensitivity. As a result of this extremely favorable property, such lamps facilitate and accelerate the working procedures in the dark room and, therefore, are finding introduction in practice to an increasing extent. A disadvantage is that the highly sensitive silver halide emulsions, especially the bromide-iodide types, are not sufficiently stable toward this comparatively bright light, and fog during the processing.

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used for radiography with and without intensifying screens. The emulsions may contain the customary macromolecular, water-permeable, organic colloid binders, emulsion additives such as hardeners, wetting agents, development accelerators, antifoggants, etc. Especially favorable sensitometric processing results can be achieved if, according to the invention, poly(alkylene oxide) compounds with a molecular weight of preferably 1500-4000 and more are added to the emulsion as part of the sensitizing system. Suitable poly(alkylene glycols) as well as their condensation products with acids, alcohols or amides and macromolecular water-permeable organic colloid binders are described in U.S. Pats. 2,240,472, 2,400,532, 2,423,549, 2,441,389, 2,955,037 and 2,965,487. As is known, the action of these poly(alkylene oxide) compounds increase the developing speed or, for the same given developing times, increase the sensitivity of the emulsion. Surprisingly, combinations of poly(alkylene oxide) compounds and the materials described herein produce high sensitivity values in substantially shorter time without the appearance of fog characteristic of these long-chain compounds.

The invention is illustrated, but not restricted, by the following examples:

## EXAMPLE 1

An optically unsensitized, highly sensitive silver halide emulsion is produced containing about 5% gelatin and about 10% silver halide. The silver halide consists of 98 weight percent AgBr and 2 weight percent of silver iodide. Added to this emulsion per mole of silver halide are

0.03 g. diphenyldisulfide-2,2'-dicarboxylic acid  
0.05 g. metol  
1.0 g. 3,3,3',3' - tetramethyl-5,6,5',6'-tetrahydroxy-spiro-bis-indane

The emulsion described above which contains none of these additives, is used for comparison. The emulsions were coated on a polyester film support and the light-sensitive material obtained was then evaluated by exposing test strips for 2 sec. with two Osram lamps (Wi 9 2660° K.) at a distance of 1.2 m. using a gray-wedge sensitometer with a wedge constant of  $D=0.15/\text{cm}$ . with filter BG3 (1.8 mm.) and BG38 (1.5 mm.) and then developing the strips for 90 sec. at 27° C. with a developer having the following composition:

Hydroquinone	30
1-phenyl-3-pyrazolidone	1
Na <sub>2</sub> SO <sub>3</sub> (anhydrous)	60
KOH	23
NaBO <sub>2</sub> ·4H <sub>2</sub> O	20
Water to 1 liter.	

The film was fixed in a customary fixing bath, subsequently washed and dried. The following results were obtained in which, for simple comparison, the values for the general sensitivity and the green sensitivity of the comparison emulsion were set equal to 100. In addition, the ratio of general sensitivity/green sensitivity (K) is given.

Sample	General sensitivity	Relative green sensitivity	General/green sensitivity (K)	Fog
Comparison emulsion	100	100	1.00	0.07
Emulsion of the invention	165	63	2.63	0.06

The following method was used to test the safe-light sensitivity of the film:

The test strips were exposed to a mercury high-pressure lamp with a line spectrum at 546 and 579 m $\mu$  at a distance of 70 cm. continuously increasing from 0 to 10 min. The samples were then developed in a metol-hydroqui-

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none developer and the exposure time required to produce a density of 0.1 above fog determined.

## EXAMPLE 2

The following constituents were added, per mole of silver bromide, to an emulsion produced according to Example 1:

0.03 g. diphenyldisulfide-2,2'-dicarboxylic acid  
0.90 g. 1-phenyl-3-pyrazolidone  
1.0 g. 3,3,3',3'-tetramethyl-5,6,5',6'-tetrahydroxy-spiro-bis-indane

The samples were then processed and evaluated analogous to the data in Example 1. The results obtained are compiled in the table:

Sample	General sensitivity	Relative green sensitivity	General/green sensitivity (K)	Fog
Comparison emulsion	100	100	1.00	0.07
Emulsion of the invention	165	64	2.43	0.04

## EXAMPLE 3

The following constituents were added, per mole of silver bromide, to an emulsion produced according to the data in Example 1:

0.03 g. diphenyldisulfide-2,2'-dicarboxylic acid  
0.05 g. metol  
1.00 g. 3,3,3',3'-tetramethyl-5,6,5',6'-tetrahydroxy-spiro-bis-indane  
1.00 g. carbowax 4000<sup>1</sup>

<sup>1</sup> Polyethylene glycol molecular weight 3000-3700.

The samples were then treated with the developer solution given in Example 1 for 60 sec. at 27° C. The results following results were obtained thereby:

Sample	General sensitivity	Relative green sensitivity	General/green sensitivity (K)	Fog
Comparison emulsion	100	100	1.00	0.07
Emulsion of the invention	145	59	2.46	0.05

## EXAMPLE 4

The following constituents were added, per mole of silver bromide, to an emulsion produced according to the data in Example 1:

0.03 g. diphenyl-2,2'-dicarboxylic acid  
0.20 g. 1-phenyl-3-pyrazolidone  
1.00 g. 3,3,3',3'-tetramethyl-5,6,5',6'-tetrahydroxy-spiro-bis-indane  
1.00 g. carbowax 4000

The samples were then treated with the developer solution given in Example 1 for 6 sec. at 27° C. The results obtained are compiled in the table:

Sample	General sensitivity	Relative green sensitivity	General/green sensitivity (K)	Fog
Comparison emulsion	100	100	1.00	0.07
Emulsion of the invention	155	63	2.40	0.04

From Examples 3 and 4, it is evident that in the presence of poly(ethylene oxide) compounds, the increase in sensitivity can be reached even with shorter processing times.

## EXAMPLE 5

To demonstrate the mode of action of the described combination, the compounds of the invention were added, individually and in combination with one another, to the

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light-sensitive emulsion described in Example 1. The individual compounds are indicated as follows:

I—Poly(ethylene oxide) compound (carbowax 4000)

II—Diphenyldisulfide-2,2'-dicarboxylic acid

IIIa—Metol

IIIb—1-phenyl-3-pyrazolidone

IV—3,3,3',3'-tetramethyl-5,6,5',6'-tetrahydroxy-spiro-bis-indane

The results obtained on processing with the developer solution given in Example 1 with a developing time of 90 sec. at 27° C. are compiled in the table:

Grams of substance introduced per mole AgBr					General sensitivity	Relative green sensitivity	General/green sensitivity	Fog
I	II	IIIa	IIIb	IV				
0	0	0	0	0	100	100	1.00	0.07
1	0	0	0	0	120	143	0.84	0.11
0	0	0	0	1	106	67	1.58	0.05
1	0	0	0	1	130	72	1.80	0.05
0	0.03	0	0	1	100	67	1.50	0.05
0	0	0	0.9	1	127	51	2.50	0.06
0	0	0.05	0	1	115	53	2.20	0.05
1	0.03	0	0	0	145	91	1.60	0.08
0	0.03	0.05	0	0	165	77	2.15	0.07
0	0.03	0	0.8	0	145	82	1.77	0.08
1	0.03	0	0.9	0	145	82	1.77	0.10
1	0.03	0.05	0	0	175	77	2.28	0.11
1	0	0.05	0	1	135	59	2.29	0.06
1	0.03	0	0	1	141	65	2.17	0.05
0	0.03	0.05	0	1	165	63	2.62	0.05
0	0.03	0	0.3	1	145	59	2.46	0.05
0	0.03	0	0.9	1	155	63	2.46	0.04
1	0.03	0.05	0	1	185	61	3.05	0.07
1	0.03	0	0.9	1	195	56	3.48	0.07

The great advantage of this invention is that it offers the possibility of producing emulsions for radiography with intensifying screens, the sensitivity of which can be increased selectively in the blue region of the spectrum, while at the same time reducing the sensitivity in the long-wave region, especially in the adjacent green region, so that these emulsions can be processed in high-intensity green safe lights without deleterious side effects. An additional advantage is that the combination described is characterized as being very stable so that emulsions with an improved sensitivity/fog ratio can be obtained. In the presence of poly(alkylene oxide) compounds, this improved sensitivity/fog ratio is achieved at substantially shorter developing times.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. Optically unsensitized, highly sensitive photographic silver halide emulsion, characterized in that it contains a diphenyldisulfidedicarboxylic acid, a polyhydroxy-spiro-bis-indane and a p-aminophenol or a 3-pyrazolidone developing agent.

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2. Silver halide emulsion according to claim 1, characterized in that it contains diphenyldisulfide-2,2'-dicarboxylic acid.

3. Silver halide emulsion according to claim 1, characterized in that it contains 3,3,3',3'-tetramethyl-5,6,5',6'-tetrahydroxy-spiro-bis-indane.

4. Silver halide emulsion according to claim 1, characterized in that it contains N-methyl-p-aminophenol.

5. Silver halide emulsion according to claim 1, characterized in that it contains 1-phenyl-3-pyrazolidone.

6. Silver halide emulsion according to claim 1, characterized in that, in addition, it contains a polyethylene

glycol compound with a molecular weight of at least 1500.

7. A silver halide emulsion according to claim 1, wherein the constituents are present in the amounts 0.015–0.120, 0.5–1.50, 0.01–0.10, and 0.05–1.0 gram, respectively, per mole of silver halide.

8. An emulsion according to claim 7 which is a gelatino-silver bromide-iodide emulsion.

#### References Cited

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