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3,506,451

DIRECT POSITIVE PHOTOGRAPHIC MATERIALS

Nobuo Soma, Junichi Nakazawa, Yoshio Sato, and Yoshimi Kuwabara, Tokyo, and Hidehiko Ishikawa, Odawara-shi, Japan, assignors to Sankyo Co., Ltd., and Konishiroku Photo Industry Co., Ltd., both of Tokyo, Japan, both corporations of Japan

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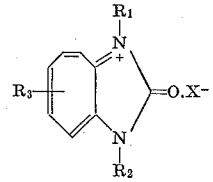
Int. Cl. G03c 1/36
U.S. Cl. 96—101 11 Claims

ABSTRACT OF THE DISCLOSURE

A direct positive photographic element comprising a fog silver halide emulsion containing as a deep sensitizer 1,3 substituted-2,3-dihydro-2 oxocycloheptimidazolium salts.

This invention relates to a direct positive light-sensitive silver halide photographic material which comprises a support and, coated thereon, a light-sensitive silver halide emulsion layer containing fogged silver halide crystals, said layer having a desensitizer incorporated therein, said desensitizer being a compound represented by the general formula



(I)

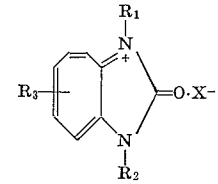
wherein R_1 is alkyl, substituted or unsubstituted aryl, or substituted or unsubstituted aralkyl radical; R_2 is substituted or unsubstituted aryl radical or substituted or unsubstituted aralkyl radical; R_3 is hydrogen, halogen, alkyl or phenyl radical; and X^- is an anion. It is the principal object of the invention to provide a direct positive, light-sensitive silver halide photographic material having high reversal sensitivity and high contrast and being free from any staining of photographic surface.

A direct positive, light-sensitive silver halide photographic material of the kind specified, which comprises a fogged silver halide emulsion, can directly yield a positive image through a single exposure and single development by utilization of Herschel effect, solarization, dye reversal (spectrally sensitized reversal), etc. In order to accelerate these actions, it is well known to incorporate an appropriate desensitizer into the fogged silver halide emulsion before coating.

Heretofore, a number of compounds have been known useful as desensitizers for direct positive light-sensitive silver halide photographic materals, which compounds include, for example, phenosafranine, malachite green, pinacryptol yellow, pinacryptol green, etc. These known desensitizers suffer from several drawbacks and are not satisfactory in their actual use. For instance, phenosafranine which is a substance having red color usually causes reddish coloration of the photographic materials, sometimes wtih decrease in contrast. Marachite green and pinacryptol green, both of which are green compounds, will decrease whiteness of the background of photographic pictures. Furthermore, pinacryptol green sometimes has an adverse effect against stability of a fogged emulsion. Pinacryptol yellow, which is a generally preferred known desensitizer because of its raising no problem in contrast of photographic images, will cause yellowish coloration to decrease whiteness of the surface

of photographic materials. Thus, all the known desensitizers are not satisfactory because of their undesired influence on the photographic properties.

We have now found that a compound of the general formula



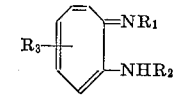
(I)

wherein R_1, R_2, R_3 and X^- are defined as above can be used as a densitizer for a direct positive, light-sensitive silver halide photographic material, without causing any contamination or coloration of photographic images and any adverse influence on the photographic properties. Thus, in accordance with the present invention, there is provided a direct positive, light-sensitive silver halide photographic material which comprises a light-sensitive silver halide emulsion layer containing fogged silver halide crystals and having a compound of the above general formula, as a desensitizer, incorporated therein.

The compounds defined above are available at relatively low costs. Almost all of these are colorless substances, but a few have a very sight color insufficient to cause coloration. The compounds can meet the following requirements:

(1) They have a capability to decrease photographic sensitivity;
(2) They do not cause fogging or decrease in contrast;
(3) They do not cause any adverse effect on fogged silver halide crystals;
(4) They can accelerate Herschel effect, solarization and dye reversal, and markedly improve the sensitivity of a direct positive light-sensitive photographic material; and
(5) They are water-soluble.

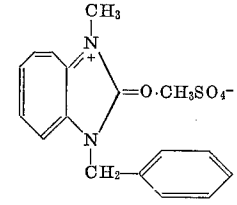
A compound of the above general formula can be prepared according to the method described in "Chemical & Pharmaceutical Bulletin" vol. 13, No. 7, pages 819–820, that is by the reaction of a troponeimine derivative of the formula



wherein R_1, R_2 and R_3 are defined as above with a compound of the formula X'COOR' wherein R' is alkyl and X' is halogen. If a compound of the above general Formula I, wherein the anion X^- is other than halogen, is desired, it can be obtained as by treating 1,3-disubstituted-2-oxocycloheptimidazolium halogenide with an appropriate acid (e.g. sulfuric acid, methylsulfuric acid, etc.).

Typical compounds comprehended by the present invention are as follows:

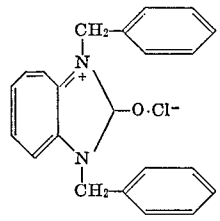
(1)



M.P. 182° C.

1-methyl-3-benzyl-2,3-dihydro-2-oxocycloheptimidazolium monomethylsulfate

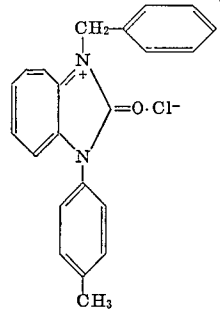
(2)



M.P. 237° C.

1,3-dibenzyl-2,3-dihydro-2-oxocycloheptimidazolium

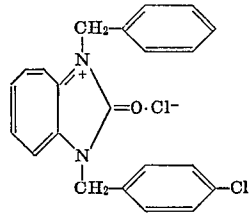
(3)



M.P. 225° C. (decomp.)

1-benzyl-3-(p-tolyl)-2,3-dihydro-2-oxocycloheptimidazolium chloride

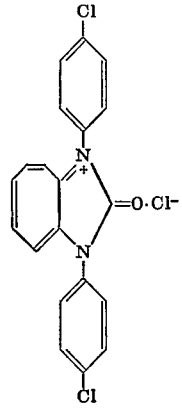
(4)



M.P. 236° C. (decomp.)

1-benzyl-3-(p-chlorobenzyl)-2,3-dihydro-2-oxocycloheptimidazolium chloride

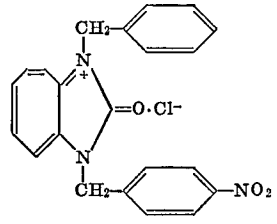
(5)



M.P. 241° C. (decomp.)

1,3-di(p-chlorophenyl)-2,3-dihydro-2-oxocycloheptimidazolium chloride

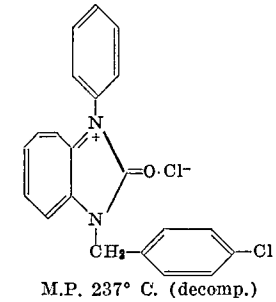
(6)



M.P. 2370° C. (decomp.)

1-benzyl-3-(p-nitrobenzyl)-2,3-dihydro-2-oxocycloheptimidazolium chloride

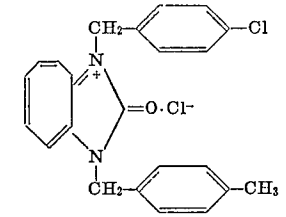
(7)



M.P. 237° C. (decomp.)

1-phenyl-3-(p-chlorobenzyl)-2,3-dihydro-2-oxocycloheptimidazolium chloride

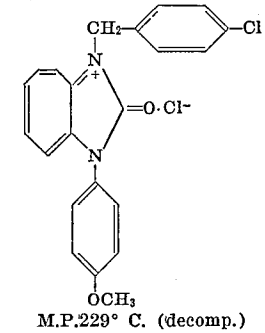
(8)



M.P. 230° C. (decomp.)

1-(p-chlorobenzyl)-3-(p-methylbenzyl)-2,3-dihydro-2-oxocycloheptimidazolium chloride

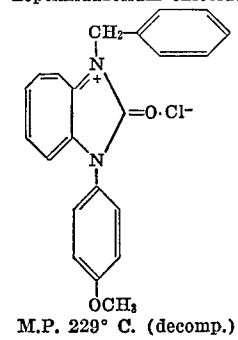
(9)



M.P.229° C. (decomp.)

1-(p-chlorobenzyl)-3-(p-anisyl)-2,3-dihydro-2-oxocycloheptimidazolium chloride

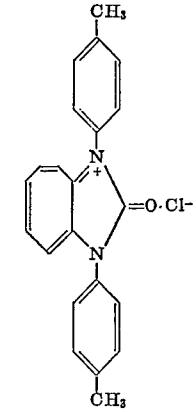
(10)



M.P. 229° C. (decomp.)

1-benzyl-3-(p-anisyl)-2,3-dihydro-2-oxocycloheptimidazolium chloride

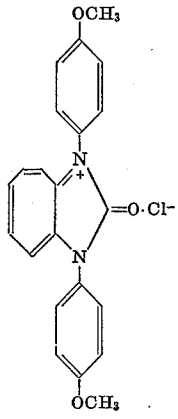
(11)



M.P. 261° C.

1,3-di(p-tolyl)-2,3-dihydro-2-oxocycloheptimidazolium chloride

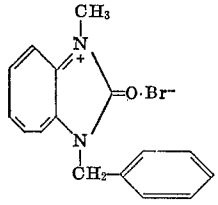
(12)



M.P. 275° C.

1,3-di(p-anisyl)-2,3-dihydro-2-oxocycloheptimidazolium chloride

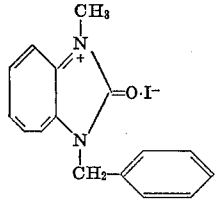
(13)



M.P. 249° C.

1-methyl-3-benzyl-2,3-dihydro-2-oxocycloheptimidazolium bromide

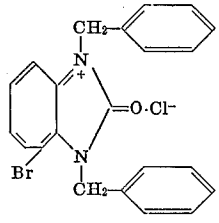
14)



M.P. 233° C.

1-methyl-3-benzyl-2,3-dihydro-2-oxocycloheptimidazolium iodide

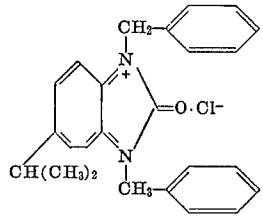
(15)



M.P. 232° C. (decomp.)

1,3-dibenzyl-6-bromo-2,3-dihydro-2-oxocycloheptimidazolium chloride

(16)



M.P. 123° C. (decomp.)

1,3-dibenzyl-5-isopropyl-2,3-dihydro-2-oxocyclo-heptimidazolium chloride

In carrying out the invention in practice, any one of the above-illustrated compounds can be incorporated into a light-sensitive silver halide photographic emulsion containing fogged silver halide crystals. Formation of the fogged silver halide crystals can be made in the manner known per se. The silver halide may be any of the silver chloride, silver chlorobromide and silver chloroiodide. Suitable amounts of the compound to be used as a desensitizer will be within the range of 0.005 to 0.5 g. per 100 g. of silver nitrate, the amount of which is calculated from the silver halide contained in the emulsion. However, this is not so a strict range and it is possible, without any adverse effect, to use an amount slightly outside of said range. Usually it is preferred to dissolve the desensitizer in water, or a water-miscible organic solvent (e.g. a lower alcohol or acetone) or the mixture of both to have a solution which is then added to the emulsion containing fogged silver halide crystals. Other suitable additives or adjuvants, e.g. stabilizer, coating aid, film hardener, matting agent, etc., can be used in combination with the desensitizer. The thus prepared emulsion is coated on a suitable support in the manner known per se and then dried, thereby to obtain a direct positive, light-sensitive silver halide photographic material, which is entirely free from any staining or coloration of photographic surfaces and which can yield a very clear positive image with high contrast and with high whiteness of the reversed portion.

The following examples describe certain ways in which the principle of the invention has been applied, but are not to be construed as limiting its scope.

EXAMPLE 1

One kilogram of a pure silver chloride emulsion containing the equivalent to 40 g. of silver nitrate was buffered to pH 8.0 by the addition of 30 ml. of 6% aqueous sodium metaborate solution. This emulsion was added further with 7 ml. of 3% formalin and heated at 50° C. for 60 minutes. The thus fogged emulsion was buffered to pH 6.0 with 10% aqueous citric acid solution and then divided to ten portions, each of which was added with the compound indicated in Table 1. The respective portions were coated on photographic papers and then dried. The thus prepared ten direct positive, light-sensitive photographic sheets were subjected to stepwise exposure to light through a filter (Toshiba UY–47) which can pass a light having a wave length of longer than 450 mμ and then treated by development under fully same condition. The sensitometric results obtained are set forth below:

TABLE 1

Compound added	Amount added mg.	Reversal photographic speed	Photographic gamma	Reversal minimum density
Pinacryptol yellow	10	100	3.50	<0.01
Phenosafranine	10	92	3.00	0.01
Compd. (2)	10	110	3.60	<0.01
Compd. (3)	10	116	3.58	<0.04
Compd. (4)	10	115	3.66	<0.01
Compd. (5)	10	108	3.55	<0.01
Compd. (6)	10	107	3.60	<0.01
Compd. (7)	10	118	3.64	<0.01
Compd. (9)	10	110	3.55	<0.01
Compd. (10)	10	116	3.57	<0.01

As apparent from the above, the sheets according to the present invention were more excellent in the reversal sensitivity and contrast than the control sheets. In addition, the sheets of the invention were entirely safe from coloration, whereas the control sheet loaded with pinacryptol yellow or safranine suffered from yellowish or reddish coloration.

EXAMPLE 2

One kilogram of a silver chloroiodide emulsion containing the equivalent to 40 g. of silver nitrate was buffered to pH 7.5 by the addition of 25 cc. of 5% aqueous sodium carbonate solution. 10 ml. of 3% formalin was also added thereto and the resulted emulsion was heated at 55° C. for 40 minutes. The fogged emulsion was divided to ten portions, each of which was added with the compound indicated in Table 2. The respective portions were coated on photographic papers and then dried. The thus prepared ten direct positive, light-sensitive photographic sheets were subjected to imagewise exposure to white light and then

treated with a developing solution. The sensitometric results obtained are set forth below:

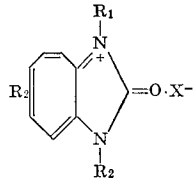
TABLE 2

Compound added	Amount added mg.	Reversal photographic speed	Photographic gamma	Reversal minimum density
Pinacryptol yellow	15	900	3.55	0.06
Phenosafranine	15	720	2.80	0.09
Compd. (2)	15	1,120	3.74	<0.01
Compd. (3)	15	1,150	3.75	<0.01
Compd. (4)	15	1,140	3.68	<0.01
Compd. (5)	15	1,075	3.65	0.01
Compd. (6)	15	1,090	3.70	0.01
Compd. (7)	15	1,210	3.75	<0.01
Compd. (9)	15	1,095	3.65	0.01
Compd. (10)	15	1,120	3.69	0.01

As apparent from the above table, the sheets according to the present invention were more excellent in the reversal sensitivity and contrast than the control sheets and further they were entirely safe from any coloration.

What we claim is:

1. A direct positive, light-sensitive silver halide photographic material which comprises a support and, coated thereon, a light-sensitive silver halide photographic emulsion layer containing fogged silver halide crystals and a desensitizing amount of a compound of the general formula



wherein R_1 is alkyl, substituted or unsubstituted aryl or substituted or unsubstituted aralkyl; R_2 is substituted or unsubstituted aryl or substituted or unsubstituted aralkyl; R_3 is hydrogen, halogen, alkyl or phenyl; and X^- is an anion.

2. A direct positive, light-sensitive silver halide photographic material as claimed in claim **1**, wherein R_1 and R_2 are benzyl, R_3 is hydrogen and X^- is chloride.

3. A direct positive, light-sensitive silver halide photographic material as claimed in claim **1**, wherein R_1 is p-chlorobenzyl, R_2 is p-methoxybenzyl, R_3 is hydrogen and X^- is chloride.

4. A direct positive, light-sensitive silver halide photographic material as claimed in claim **1**, wherein R_1 is benzyl, R_2 is p-methoxybenzyl, R_3 is hydrogen and X^- is chloride.

5. A direct positive, light-sensitive silver halide photographic material as claimed in claim **1**, wherein R_1 is benzyl, R_2 is p-tolyl, R_3 is hydrogen and X^- is chloride.

6. A direct positive, light-sensitive silver halide photographic material as claimed in claim **1**, wherein R_1 is benzyl, R_2 is p-chlorobenzyl, R_3 is hydrogen and X^- is chloride.

7. A direct positive, light-sensitive silver halide photographic material as claimed in claim **1**, wherein both of R_1 and R_2 are p-chlorophenyl, R_3 is hydrogen and X^- is chloride.

8. A direct positive, light-sensitive silver halide photographic material as claimed in claim **1**, wherein R_1 is benzyl, R_2 is p-nitrobenzyl, R_3 is hydrogen and X^- is chloride.

9. A direct positive, light-sensitive silver halide photographic material as claimed in claim **1**, wherein R_1 is phenyl, R_2 is p-chlorobenzyl, R_3 is hydrogen and X^- is chloride.

10. A direct positive, light-sensitive silver halide photographic material as claimed in claim **1**, wherein R_1 is p-chlorobenzyl, R_2 is p-methylbenzyl, R_3 is hydrogen and X^- is chloride.

11. A direct positive, light-sensitive silver halide photographic material as claimed in claim **1**, wherein both of R_1 and R_2 are p-tolyl, R_3 is hydrogen and X^- is halide.

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NORMAN G. TORCHIN, Primary Examiner

R. E. FICHTER, Assistant Examiner

U.S. Cl. X.R.

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