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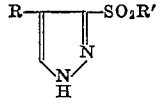
LIGHT-SENSITIVE SILVER HALIDE EMULSION CONTAINING A PYRAZOLE COMPOUND ANTIFOGGANT

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ABSTRACT OF THE DISCLOSURE

A pyrazole compound having the general formula

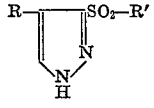


wherein R and R′ are individually selected from the group consisting of phenyl, lower alkyl substituted phenyl, lower alkoxy substituted phenyl or halogen substituted phenyl is incorporated into a light-sensitive silver halide photographic material. The pyrazole compound may be used in an amount of 10 mg. to 2 g. per mole of silver halide contained in the photographic material. A light-sensitive silver halide photographic material which is essentially free from formation of fog and stain and which has good stability is obtained.

This invention relates to a process for producing a light-sensitive silver halide photographic material (hereinafter referred to as "a photographic material") which is substantially free from fog and stain and has good stability.

It is well known that a light-sensitive silver halide photographic material usually suffers from decreased sensitivity or fogging during its storage over a long period of time. In order to allevate the above defect, it is commonly adopted to incorporate a suitable stabilizer into the light-sensitive silver halide photographic material. In the current techniques, high temperature development has been developed for rapid processing of a light-sensitive silver halide photographic material. However, such high temperature development usually accelerates fogging or color staining with causing deterioration of a light-sensitive silver halide photographic material in color balance. For the above reasons, there has strongly been desired the advent of a light-sensitive silver halide photographic material which is free from formation of such fog and stain.

We have found that a new pyrazole compound of the general formula



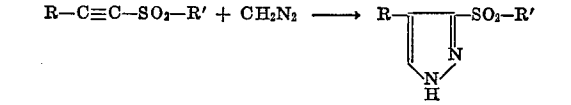
wherein R and R′, which may be same or different, are individually a phenyl group which may be substituted with a lower alkyl group, a lower alkoxy group or a halogen atom, is particularly effective as antifoggant, and have been successful in producing a light-sensitive silver halide photographic material which is essentially free from formation of fog and stain and has good stability.

In accordance with the present invention, there is provided a process for producing a light-sensitive silver halide photographic material, characterized in that a pyrazole compound of the above-mentioned general formula is incorporated into at least one layer constituting said photographic material.

Typical examples of the pyrazole compound of the above-mentioned general formula are as follows:

Compound Number	Name	Melting point, ° C.
(I)	3-(p-tolylsulfonyl)-4-phenylpyrazole	167.5–168.5
(II)	3-(p-tolylsulfonyl)-4-(p-bromophenyl) pyrazole.	162–163
(III)	3-(p-tolylsulfonyl)-4-(p-tolyl) pyrazole	156–158
(IV)	3-(p-tolylsulfonyl)-4-(m-methoxyphenyl) pyrazole.	107–109

The above-mentioned pyrazole compounds are novel and can be obtained by reacting a sulfonated acetylene compound with diazomethane as shown by the following reaction equation:



wherein R and R′ are as defined above.

REFERENTIAL SYNTHESIS EXAMPLE

100 grams of p-tolylsulfonyl phenylacetylene is dissolved in 100 ml. of ether, and the resulting solution is cooled to 5° C. Into this solution is dropped 369 ml. (4.65 mg./ml.) of an ether solution of diazomethane, and the resulting mixture is stirred at 5° C. for 5 hours and then allowed to stand overnight at room temperature. Subsequently, the solvent is removed by distillation from the reaction mixture, and the residue is recrystallized from ethyl acetate, whereby 3-(p-tolylsulfonyl)-4-phenylpyrazole can be obtained.

In practicing the present inventoin, it is effective to incorporate the pyrazole compound into at least one of the emulsion layer, inter layer, protective layer and backing layer which constitute a light-sensitive silver halide photographic material, but it is most preferable to add the pyrazole compound to a photographic emulsion which has completed the second ripening. Alternatively, the compound may be added either before or during the second ripening to control the progress of ripening, or may have previously been incorporated into gelatin or the like materials for preparing the emulsion. Of course, it is also possible to incorporate the compound into a color photographic emulsion which may contain a color coupler having a long-chain alkyl group as diffusion-preventing group. Further, the pyrazole compound may be incorporated into a color photographic emulsion according to the so-called protect type process by dissolving the pyrazole compound and a water-insoluble or sparingly water-soluble color former in a water-immiscible or sparingly water-miscible high boiling solvent and then dispersing the resulting solution into a photographic emulsion.

The amount of said pyrazole compound to be added varies depending on the kind of emulsion and the conditions for desired fog inhibition. Generally, however, 10 mg. to 2 g. of the pyrazole compound per mol of silver halide may be added in the form of a solution in a suitable organic solvent such as, for example, methanol, ethanol, acetone or ethyl acetate. In case the pyrazole compound is desired to be incorporated into other layer than the emulsion layer, the amount of the compound may be so controlled that after preparation of the photographic material, the total amount thereof per unit area corresponds to the above-mentioned amount and, in some cases, the amount of the pyrazole compound may be increased properly.

The photographic emulsion used in the present invention may have been subjected to chemical sensitization such as gold or sulfur sensitization and/or optical sensitization. The pyrazole compound of the present invention not only does not injure the sensitivity increase attained by said sensitization but also can further inhibit the increase of fog occasionally observed in such sensitization. Further, the photographic emulsion may have been incorporated with stabilizers, surfactants and hardeners.

The present invention is illustrated in further detail below with reference to examples, in which the compounds of the invention are represented by the numbers of the previously exemplified compounds.

EXAMPLE 1

A high speed silver iodobromide emulsion was subjected to ordinary chemical ripening. To this emulsion were added 50 mg. per 100 ml. of the silver halide of 5-methyl-7-hydroxy-s-triazolo(2,3-a) pyrimidine as a stabilizer and 1 g. of saponin as a coating aid. Thereafter, the emulsion was incorporated with a given amount of each of the pyrazole compounds of the present invention, and then coated on a cellulose triacetate film base, followed by drying, to prepare a photographic film. This film was exposed to light according to the JIS method K7609, and then developed at 30° C. for 90 seconds, 35° C. for 40 seconds and 40° C. for 25 seconds by use of a strongly alkaline developing solution (so-called PQ developer) containing 1-phenyl-3-pyrazolidone-hydroquinone to measure the speed and fog density thereof. The results obtained were as set forth in Table 1.

TABLE 1

No. of incorporated compound	Incorporated [1]	30° C., 90 seconds		35° C., 40 seconds		40° C., 25 seconds	
		Relative speed	Fog	Relative speed	Fog	Relative speed	Fog
(I)	190	100	0.06	100	0.12	100	0.13
(II)	190	95	0.07	100	0.12	100	0.18
(III)	190	95	0.06	100	0.10	100	0.18
(IV)	190	100	0.06	100	0.12	100	0.16
Nonincorporation		100	0.20	100	0.45	100	0.80

[1] Amount per 0.56 mol of silver halide (mg.).

From Table 1, it is understood that even when subjected to high temperature development, the photographic films incorporated with the pyrazole compounds of the present invention were not deteriorated in speed and were inhibited from formation of fog.

EXAMPLE 2

To a green-sensitive, high speed silver iodobromide color photographic emulsion were added 20 mg. per 100 ml. of the silver halide of 5-methyl-7-hydroxy-s-triazolo (2,3-a)-pyrimidine as a stabilizer and a 1 N-caustic soda solution containing 15 g. of 1-(4-carboxyphenyl)-3-(4-palmitoylaminobenzoylamino) - 5 - pyrazolone (magenta coupler), and the emulsion was adjusted to pH 6.8 by the addition of citric acid. The thus treated emulsion was incorporated with a given amount of each of the pyrazole compounds of the present invention, and then coated on a film base, followed by drying, to prepare a color film. This color film was developed at 23° C. for 9 minutes and at 25° C. for 6 minutes by use of a color developing solution containing diethyl-p-phenylenediamine, and then subjected to water-washing, bleaching, water-washing, fixing, water-washing and drying in succession to measure the speed and fog density thereof. The results obtained were as shown in Table 2.

TABLE 2

No. of incorporated compound	Incorporated amount per liter of emulsion (mg.)	23° C., 9 minutes		25° C., 6 minutes	
		Relative speed	Fog	Relative speed	Fog
(I)	150	100	0.02	100	0.05
(II)	150	100	0.02	100	0.05
(III)	150	95	0.02	95	0.04
(IV)	150	100	0.02	100	0.04
Nonincorporation		100	0.10	100	0.18

As seen in Table 2, the color films incorporated with the pyrazole compounds of the present invention could inhibit color fog formed at the time of color development.

EXAMPLE 3

To a red-sensitive silver iodobromide color photographic emulsion containing 25 mol percent of silver bromide were added 100 mg. per liter of the silver halide of 5-methyl-7-hydroxy-s-triazolo(2,3-a) pyrimidine as a stabilizer and a 1 N-caustic soda solution containing 20 g. of 1-hydroxy-4-sulfo-naphthoic acid octadecylamide (cyan coupler), and the emulsion was adjusted to pH 6.5 by the addition of citric acid. The thus treated emulsion was incorporated with a given amount of each of the pyrazole compounds of the present invention, and then coated on a photographic paper base, followed by drying, to prepare a color photographic paper. This photographic paper was developed at 28° C. for 4 minutes by use of a color developing solution containing p-aminoethyl-hydroxyethylaniline, and then subjected to fixing, water-washing, bleaching, fixing, water-washing and drying to measure the speed and fog density thereof. The results obtained were as shown in Table 3.

TABLE 3

No. of incorporated compound	Incorporated amount per liter of emulsion (mg.)	28° C., 4 minutes	
		Relative speed	Fog
(I)	120	100	0.02
(II)	120	100	0.03
(III)	120	100	0.02
(IV)	120	100	0.02
Nonincorporation		100	0.09

As seen in Table 3, the photographic papers incorporated with the pyrazole compounds of the present invention could inhibit color fog formed at the time of color development and gave no detrimental effect to speed.

EXAMPLE 4

To the high speed silver iodobromide emulsion used in Example 1 was added 2 mg. of sodium thiosulfate per liter of the silver halide as a sulfur sensitizer, and the emulsion was subjected to ordinary chemical ripening. The thus treated emulsion was incorporated with a given amount of each of the pyrazole compounds of the present invention and then formed into a film. This film was stored at 55° C. for 3 days and at 55° C. and 80% RH for 3 days. Thereafter, the film was treated in the same manner as in Example 1 to measure the speed and fog density thereof. The results obtained were as shown in Table 4.

TABLE 4

No. of incorporated compound	Incorporated [1]	Immediately after preparation		After incubation at 55° C. for 3 days		After incubation at 55° C. 80% RH for 3 days	
		Relative speed	Fog	Relative speed	Fog	Relative speed	Fog
(I)	180	100	0.03	90	0.18	80	0.19
(II)	180	100	0.02	97	0.18	80	0.19
(III)	180	100	0.03	95	0.18	85	0.16
(IV)	180	100	0.05	85	0.30	82	0.42
Non-incorporation		100	0.05	40	0.65	5	0.95

[1] Amount per 0.56 mol of silver halide (mg.).

As seen in Table 4, the films incorporated with the pyrazole compounds of the present invention were not injured in speed and could inhibit the formation of fog.

EXAMPLE 5

A 3% aqueous gelatin solution was incorporated with a 2% methanol solution of each of the pyrazole compounds of the present invention and further with 20 cc. of a 5% saponin solution as a coating aid. The thus treated gelatin solution was coated as a protective layer on a high speed roentgen film and then dried. This film was subjected to high temperature development in the same manner as in Example 1 to measure the speed and fog density thereof. The results obtained were as shown in Table 5.

TABLE 5

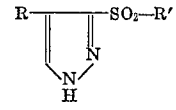
No. of incorporated compound	Incorporated [1]	30° C., 90 seconds		35° C., 40 seconds		40° C., 25 seconds	
		Relative speed	Fog	Relative speed	Fog	Relative speed	Fog
(I)	300	105	0.07	100	0.12	100	0.20
(II)	300	100	0.10	100	0.18	100	0.31
(III)	300	95	0.08	100	0.10	100	0.20
(IV)	300	100	0.07	100	0.12	100	0.20
Non-incorporation		100	0.19	100	0.33	100	0.56

[1] Amount per liter of 3% gelatin (mg.).

From Table 5, it is understood that even when incorporated into a protective layer, the pyrazole compounds of the present invention successfully inhibited the formation of fog due to high temperature development and showed excellent photographic characteristics without giving any detrimental effect to speed.

What we claim is:

1. A photo-sensitive silver halide element having incorporated therein an antifogging concentration of a pyrazole compound of the general formula,



wherein R and R', which may be same or different, are individually a phenyl group which may be substituted with a lower alkyl group, a lower alkoxy group or a halogen atom.

2. The element as claimed in claim 1, wherein said element contains a color coupler.

3. The element as claimed in claim 1, wherein said pyrazole compound is selected from the group consisting of 3-(p-tolylsulfonyl-4-phenylpyrazole, 3-(p-tolylsulfonyl)-4-(p-bromophenyl)pyrazole, 3-(p-tolylsulfonyl)-4-(p-tolyl)-pyrazole and 3-(p-tolylsulfonyl)-4-(m-methoxypheny)pyrazole.

4. The element as claimed in claim 1, wherein the element contains 10 mg. to 2 g. of said pyrazole compound per mol of silver halide.

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