United States Patent Office

3,813,250

Patented May 28, 1974

3,813,250

SILVER HALIDE PHOTOSENSITIVE ELEMENT CONTAINING AN ANTIFOGGING COMBINATION OF A NITRATED HETEROCYCLIC COMPOUND AND A POLYMERIC STABILIZER

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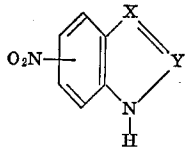
No Drawing. Filed Oct. 10, 1972, Ser. No. 296,492
Claims priority, application Japan, Oct. 11, 1971, 46/79,979
Int. Cl. G03c 1/34
U.S. Cl. 96—76 R 15 Claims

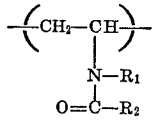
ABSTRACT OF THE DISCLOSURE

Anti-fogging agents for silver halide photographic emulsions consisting of a combination of (a) an nitrated benzimidazole, indazole or benzotriazole compound represented by the general formula



(I)

where X and Y individually represent N or CR, wherein R represents a hydrogen atom or alkyl group containing 1 to 4 carbon atoms, and (b) at least one member selected from polymers containing greater than 50 mol percent of recurring units represented by the general formula



(II)

wherein R_1 and R_2 individually represent a hydrogen atom or an alkyl group containing 1 to 4 carbon atoms or form, when taken together with the nitrogen and carbon atoms to which they are attached, a 5- to 7-membered heterocyclic ring.

The anti-fogging agent may be incorporated in silver halide emulsion layers or in another layer adjacent to the emulsion layer to reduce fog in the emulsion layer without a sacrifice in the sensitivity of the photosensitive materials.

BACKGROUND OF THE INVENTION

Field of the invention

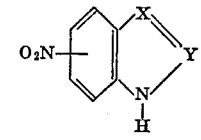
This invention relates to silver halide photosensitive materials, in particular, to silver halide photosensitive materials improved in sensitivity and fog.

Description of the prior art

A variety of anti-fogging compounds have been incorporated into silver halide photographic emulsions to reduce fog. However, the minimization of fog in this way is usually accompanied by a noticable lowering of sensitivity. To say, it is difficult to sufficiently reduce fog without a sacrifice in sensitivity.

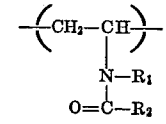
Summary of the invention

We have now discovered that it is possible to remarkably reduce fog with a minimum reduction in sensitivity by incorporating into photographic emulsions a combination of (a) a compound represented by general formula (I)



(I)

wherein X and Y individually represent N or CR wherein R represents a hydrogen atom or an alkyl group containing 1 to 4 carbon atoms; and (b) at least one member selected from polymers containing greater than 50 mol percent of the recurring unit represented by the general formula

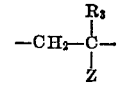


(II)

wherein R_1 and R_2 individually represent a hydrogen atom or an alkyl group containing 1 to 4 carbon atoms or form, when taken together with the nitrogen and carbon atoms to which they are attached, a 5- to 7-membered heterocyclic ring such as, for example, pyrrolidone, piperidone and caprolactam.

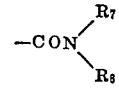
The polymers within the scope of the general formula (II) include homopolymers composed of the recurring unit represented by the formula (II); copolymers composed of two or more different recurring units represented by the formula (II); and copolymers composed of greater than 50 mol percent of at least one recurring unit represented by the formula (II) and at least one monomer which is copolymerizable with the above recurring unit.

Examples of the monomer which is copolymerizable with the recurring unit of the formula (II) include the recurring unit represented by general formula (III)



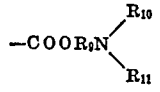
(III)

wherein R_3 represents a hydrogen atom or a methyl group, and Z represents $—OR_4$ wherein R_4 is a hydrogen atom or an alkyl group having 1 to 4 carbon atoms; $—OCOR_5$ wherein R_5 is an alkyl group having 1 to 4 carbon atoms; $—COOR_6$ wherein R_6 represents a hydrogen atom or an alkyl group having 1 to 4 carbon atoms which may be substituted with a hydroxy or an alkyl group having 1 to 4 carbon atoms;

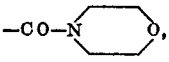


wherein R_7 and R_8 each represents a hydrogen atom or an alkyl group having 1 to 4 carbon atoms which may be substituted with a hydroxy or an alkyl group having 1 to 4 carbon atoms, or form, when taken together with the

nitrogen atom to which they are attached, a heterocyclic ring such as morpholino;



wherein R_9 represents an alkylene chain having 2 to 3 carbon atoms and R_{10} and R_{11} each represents a hydrogen atom or an alkyl group having 1 to 4 carbon atoms; —CN; an aryl group such as phenyl or sulfophenyl; Z may also be a heterocyclic ring such as pyridyl. Suitable examples of the group Z include, for example, —OH, —OCH_3, —$OCOCH_3$, —COOH, —$COOCH_3$, —$COOC_4H_9$, —$COOCH_2OH$, —$COOCH_2CH_2OCH_2CH_3$, —$CONH_2$ —$CONHC_4H_9$, —$CONHCH_2CH_2OCH_2CH_3$, —$CON(CH_2CH_2OH)_2$,



—$COOCH_2CH_2N(CH_3)_2$ and the like.

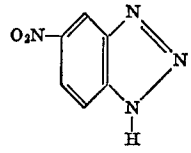
Other recurring units which are copolymerizable with the above recurring unit of the formula (II) include maleic anhydride, maleic acid, a half-ester of maleic acid, a half-amide of maleic acid and the like.

The preferred polymers are those containing vinylpyrrolidone as the recurring unit of the formula (II).

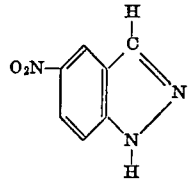
DETAILED DESCRIPTION OF THE INVENTION

The compound represented by general formula I is exemplified by the following compounds.

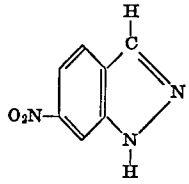
I–1 5-Nitrobenztriazole



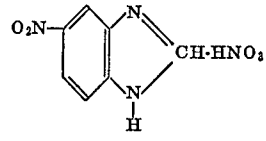
I–2 5-Nitroindazole



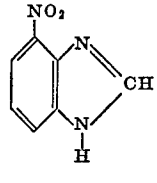
I–3 6-Nitroindazole



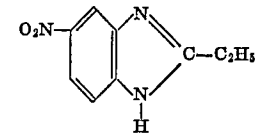
I–4 5-Nitrobenzimidazole nitrate



I–5 4-Nitrobenzimidazole



I–6 2-Ethyl-5-nitrobenzimidazole



These compounds may be synthesized by known processes as disclosed in the literature.

Homopolymers having recurring units represented by general formula II are exemplified by the following compounds.

II–1 Poly-N-vinyl-N-methylformamide
II–2 Poly-N-vinyl-N-methylacetamide
II–3 Poly-N-vinyl-N-methylpropionamide
II–4 Poly-N-vinyl-N-ethylformamide
II–5 Poly-N-vinyl-N-ethylacetamide
II–6 Poly-N-vinyl-N-ethylpropionamide
II–7 Poly-N-vinylpyrrolidone
II–8 Poly-N-vinylpiperidone
II–9 Poly-N-vinylcaprolactam

Compounds II having recurring units represented by general formula III are exemplified by the following compounds.

III–1 Copolymers of N-vinylpyrrolidone with vinyl alcohol
III–2 Copolymers of N-vinylpyrrolidone with N-methylol acrylamide
III–3 Copolymers of N-vinylpyrrolidone with N-methylacrylamide
III–4 Copolymers of N-vinylpyrrolidone with acrylonitrile
III–5 Copolymers of N-vinyl-N-methylformamide with vinyl alcohol
III–6 Copolymers of N-vinyl-N-methylformamide with acrylic acid
III–7 Copolymers of N-vinyl-N-methylformamide with vinyl acetate
III–8 Copolymers of N-vinyl-N-methylformamide with acryloylmorpholine
III–9 Copolymers of N-vinyl-N-ethylformamide with vinyl alcohol
III–10 Copolymers of N-vinyl-N-ethylformamide with acrylamide
III–11 Copolymers of N-vinyl-N-ethylformamide with acrylonitrile
III–12 Copolymers of N-vinyl-N-ethylformamide with methacrylic acid

While there is no special restriction on the molecular weight of the above homopolymers and copolymers, those preferably used have molecular weights within the range from about 4,000 to about 1,000,000, more desirably from 5,000 to 500,000 and having inherent viscosities within the range of from about 0.1 to about 3.0, more desirably 0.2 to 1.0, as determined in water at a temperature of 30° C. Homopolymers and copolymers having a molecular weight excessively lower than the above range tend to give poor results and, the other hand, those having a molecular weight excessively higher than the above range cannot easily be handled because of their high viscosity in the gelatin solution.

Compound I preferably is incorporated in an amount of from about 0.5 to about 250 mg., more desirably from 0.5 to 100 mg., per mole of silver halide contained in a silver halide emulsion, and compound II is incor-

porated in an amount of from about 0.05 to about 15 g., preferably from 0.05 to 5 g., per mole of silver halide.

It is preferred to incorporate aforesaid compounds I and II in an emulsion during the period from the second ageing to just before application of the emulsion to a support. As earlier indicated, a portion or the total amount of the compounds may be incorporated in a layer adjacent the emulsion layer. In such a case, the total amounts of each of the compounds I and II in both layers can be the same amounts as those described for the compounds I and II contained in only the emulsion layer, i.e., the total amounts of each of the compounds I and II in the emulsion layer and a layer adjacent to the emulsion layer can range from about 0.5 to about 250 mg., preferably from 0.5 to 100 mg., per mole of silver halide contained in the silver halide emulsion layer and from about 0.05 to about 15 g., preferably from 0.05 to 5 g., per mole of the silver halide contained in the silver halide emulsion layer, respectively.

The present invention is applicable to any silver halide emulsion, such as silver iodide emulsions, silver chlorobromide emulsions and silver chloroiodobromide emulsions. The emulsions may be sulfur-sensitized, gold-sensitized or reductively sensitized or may have incorporated therein spectral sensitizers, polyalkylene oxide-type sensitizers, various stabilizers, hardeners, coating assistants, couplers or like conventional adjuvants.

Any conventional support for photosensitive materials may be used in accordance with the present invention, e.g., glass, cellulose acetate films, poly(ethylene terephthalate) films, polycarbonate films, polystyrene films, polypropylene film, baryta paper and like conventional sheet materials which have been used as supports for silver halide photo-emulsions.

According to the present invention, the fog in the silver halide photosensitive materials is minimized with a minimum decrease in sensitivity.

Some embodiments of the present invention are illustrated by the following examples which are not to be taken as limitative of the invention.

EXAMPLE 1

A high sensitivity X-ray gelatin-silver iodobromide emulsion containing 1.5 mol percent of silver iodide (based on silver bromide) which was sulfur-sensitized by sodium thiosulfate and gold-sensitized by gold chloride containing 4-hydroxy-6-methyl-1,3,3a,7-tetrazoindene in an amount of 0.5 g./mol AgX, saponin in an amount of 0.5 g./mol AgX and mucochloric acid in an amount of 0.15 g./mol AgX was divided into 23 portions. To each portion was then added compounds I and II alone or in combinations of compounds I and II, in amounts as indicated in Table 1, to form an emulsion. The emulsion was applied to a poly(ethylene terephthalate) base and dried to provide a photosensitive material.

Each of the specimens thus obtained was exposed for 1/20 second through a blue filter to a light source of a color temperature of 5,400° K. and then developed at 35° C. for 25 seconds in a high pH 1-phenyl-3-pyrazolidone-hydroquinone type solution for X-ray films. The results are summarized in Table 1.

Table 1 shows that the addition of compound I alone remarkably reduces senstivity as compared with the control material and the addition of compound II alone has little effect on sensitivity. However, the addition of compound I in combination with compound II reduces fog with only a slight decrease in sensitivity.

TABLE 1

Specimen No.	Compound I No.	Compound I Amount added (mg./mol AgX)	Compound II No.	Compound II Amount added (g./mol AgX)	Relative sensitivity[1]	Fog
Control					100	0.12
A			II-7	1.35	105	0.13
B	I-1	22			75	0.07
C	I-1	55			35	0.02
D	I-1	55	II-7	0.27	55	0.02
E	I-1	55	II-7	1.35	75	0.03
F	I-1	55	II-7	2.70	95	0.05
G			II-9	1.35	105	0.13
H	I-1	55	II-9	0.27	50	0.02
I	I-1	55	II-9	1.35	60	0.02
J	I-1	55	II-9	2.70	70	0.03
K	I-1	55	II-9	5.40	90	0.05
L			III-1	1.35	100	0.12
M	I-1	55	III-1	0.27	45	0.02
N	I-1	55	III-1	1.35	55	0.02
O	I-1	55	III-1	4.05	75	0.04
P	I-1	55	III-1	6.75	95	0.07
A			II-7	1.35	105	0.13
Q	I-3	132			80	0.08
R	I-3	330			40	0.03
S	I-3	330	II-7	0.27	50	0.03
T	I-3	330	II-7	1.35	65	0.04
U	I-3	330	II-7	2.70	80	0.05
V	I-3	330	II-7	4.05	95	0.07

[1] Relative sensitivity stands for a relative value of sensitivity at the density of fog +0.3 referring to "100" as the control value.

NOTES:
II-7: $[\eta]=0.15$ (corresponding to a molecular weight of 10,000).
II-9: $[\eta]=0.37$ (corresponding to a molecular weight of 50,000).
III-1: $[\eta]=0.28$ (corresponding to a molecular weight of 30,000) a 7:3 copolymer of N-vinylpyrrolidone with vinyl alcohol.

EXAMPLE 2

The same high sensitivity X-ray gelatin-silver iodobromide emulsion as was used in Example 1 was, after the addition of a stabilizer, a wetting agent and a hardener as in Example 1, divided into 5 portions, Compound II–7 was added to certain portions, or not added, in the amounts as indicated in Table 2.

On the other hand, a 7% aqueous gelatin emulsion had added thereto saponin in an amount of 5 g./liter and mucochloric acid in an amount of 0.4 g./liter and was divided into 5 portions, and certain portions had added thereto compound I–1 in the amount indicated in Table 2. Each of the resulting solutions was applied as an adjacent layer over a layer of one of the above emulsions and dried to obtain 5 specimens. The specimens were exposed and developed under the same conditions as in Example 1 and subjected to sensitivity and fog determinations. The results obtained are summerized in Table 2.

Table 2 shows that it is possible to obtain a result similar to Example 1 by incorporating one component of the anti-fogging agent of the present invention into an emulsion layer and the other into an adjacent layer.

TABLE 2

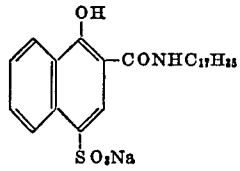
Specimen No.	Emulsion layer Compound No.	Emulsion layer Amount added (g./mol AgX)	Adjacent layer Compound No.	Adjacent layer Amount added (g./mol AgX)	Relative sensitivity	Fog
Control					100	0.12
A			I-1	60	90	0.09
B			I-1	180	60	0.06
C	II-7	0.27	I-1	180	75	0.06
D	II-7	1.35	I-1	180	95	0.07

NOTE: II-7: $[\eta]=0.87$ (corresponding to a molecular weight of 30,000).

EXAMPLE 3

A sulfur- and gold-sensitized color silver iodobromide emulsion containing silver iodide in an amount of 5 mol percent had added thereto 4-hydroxy-6-methyl-1,3,3a,7-tetrazoindene in an amount of 0.7 g./mol AgX, an alkylbenzenesulfonate in an amount of 0.8 g./mol AgX, mu-

chloric acid in an amount of 0.3 g./mol AgX and a coupler compound having the following structure in an amount of 50 mg./mol AgX:



The emulsion was then divided into 8 portions, and to each portion was added compound I or II alone or as a combination of compounds I and II in accordance with the present invention. The portions were then applied to a cellulose acetate film base and dried to provide a photosensitive film.

The film was exposed and developed in a color developing solution containing 4-amino-3-methyl-N,N-diethylaniline. The results are summerized in Table 3. Table 3 shows that the anti-fogging agent of the present invention reduces fog with only a slight decrease in sensitivity in color photographic emulsions.

TABLE 3

Specimen No.	Compound I No.	Compound I Amount added (mg./mol AgX)	Compound II No.	Compound II Amount added (g./mol AgX)	Relative sensitivity	Fog
Control					100	0.15
A			II-7	1.08	100	0.16
B	I-1	33			45	0.06
C	I-1	33	II-7	1.08	95	0.08
D	I-2	66			50	0.07
E	I-2	66	II-7	1.08	85	0.09
F	I-3	330			50	0.08
G	I-3	330	II-7	1.08	90	0.10

NOTE: II-7: $[\eta]=0.25$ (corresponding to a molecular weight of 30,000).

EXAMPLE 4

The same high sensitivity X-ray gelatin-silver iodobromide emulsion as was used in Example 1 had added thereto a stabilizer, a wetting agent and a hardener as in Example 1, and was divided into 5 portions. To each portion was added an anti-fogging compound, as listed in Table 4, and the portions then applied to a poly(ethylene terephthalate) base and dried to provide specimens. The specimens were exposed and developed under the same conditions as in Example 1 and subjected to relative sensitivity and fog determinations. The results thus obtained are summerized in Table 4. As indicated by Table 4, there were obtained silver halide photosensitive materials with a high relative sensitivity and a reduced fog, as in Example 1.

TABLE 4

Specimen No.	Emulsion layer Compound No.	Emulsion layer Amount added (mg./mol AgX)	Relative sensitivity	Fog
Control			100	0.12
A	I-1	55	35	0.02
B	I-1	55	55	0.02
	II-7	270		
C	I-1	55	45	0.02
	III-1	270		
D	I-1	55		
	II-7	80	50	0.02
	III-1	190		

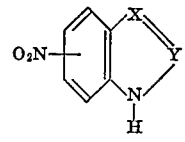
NOTES:
II-7: $[\eta]=0.15$ (corresponding to a molecular weight of 10,000).
III-1: $[\eta]=0.28$ (corresponding to a molecular weight of 30,000) a 7:3 copolymer of N-vinylpyrrolidone with vinyl alcohol.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modification can be made therein without departing from the spirit and scope thereof.

What is claimed is:

1. A silver halide photosensitive material which comprises a silver halide emulsion layer and a support, said silver halide emulsion layer further comprising:

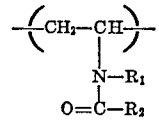
(a) a compound represented by the general formula



(I)

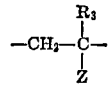
where X and Y individually represent N or CR wherein R represents a hydrogen atom or alkyl group containing 1 to 4 carbon atoms; and

(b) at least one member selected from polymers containing greater than 50 mol percent of the recurring unit represented by the general formula



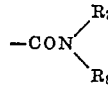
(II)

wherein R_1 and R_2 individually represent a hydrogen atom or an alkyl group containing 1 to 4 carbon atoms or form, when taken together with the nitrogen and carbon atoms to which they are attached, a 5- to 7-membered heterocyclic ring selected from the group consisting of pyrrolidone, piperidone and caprolactam, said polymers being homopolymers composed of the recurring unit represented by the formula (II); copolymers composed of two or more different recurring units represented by the formula (II); and copolymers composed of greater than 50 mol percent of at least one recurring unit represented by the formula (II) and at least one monomer which is copolymerizable with the above recurring unit, said monomer having the general formula (III)

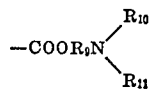


(III)

wherein R_3 represents a hydrogen atom or methyl group, and Z represents $-OR_4$ wherein R_4 is a hydrogen atom or an alkyl group having 1 to 4 carbon atoms; $-OCOR_5$ wherein R_5 is an alkyl group having 1 to 4 carbon atoms; $-COOR_6$ wherein R_6 represents a hydrogen atom or an alkyl group having 1 to 4 carbon atoms which may be substituted with hydroxy or an alkyl group having 1 to 4 carbon atoms;



wherein R_7 and R_8 each represents a hydrogen atom or an alkyl group having 1 to 4 carbon atoms which may be substituted with hydroxy or an alkyl group having 1 to 4 carbon atoms, or form, when taken together with the nitrogen atom to which they are attached, a morpholino ring;



wherein R_9 represents an alkylene chain having 2 to 3 carbon atoms and R_{10} and R_{11} each represents a hydrogen atom or an alkyl group having 1 to 4 carbon atoms; —CN; phenyl or sulfophenyl; or a pyridyl ring, the compound of general formula (I) being contained in an amount of from about 0.5 to about 250 mg. per mole of silver halide and the polymer containing greater than 50 mole percent of the recurring unit represented by the general formula (II) being contained

in an amount from about 0.05 to about 15 g. per mole of silver halide.

2. The silver halide photosensitive material as in claim 1 which further comprises a layer adjacent to said silver halide emulsion layer.

3. The silver halide photosensitive material as in claim 1 in which the copolymer having recurring units represented by general formula II is present and is contained in an amount of about 0.05 to about 15 g. per mol of silver halide.

4. The silver halide photosensitive material as in claim 1 which contains a compound represented by general formula I and a homopolymer having recurring units represented by general formula II.

5. The silver halide photosensitive material as in claim 1 which contains a compound represented by general formula I and a copolymer having recurring units represented by general formula II.

6. The silver halide photosensitive material as in claim 2 in which one of the constituent (a) and (b) is contained in the emulsion layer and the other is contained in the adjacent layer.

7. The silver halide photosensitive material as in claim 1 in which both constituents (a) and (b) are contained in the emulsion layer.

8. The silver halide photosensitive material as in claim 2 in which both constituents (a) and (b) are contained in the adjacent layer.

9. The silver halide photosensitive material as in claim 1 in which the homopolymer having recurring units represented by general formula II is present and is contained in an amount of about 0.05 to about 15 g. per mol of silver halide.

10. The silver halide photosensitive material as in claim 1 in which the compound represented by general formula (I) is selected from the group consisting of 5-nitrobenztriazole, 5-nitroindazole, 6-nitroindazole, 5-nitrobenzimidazole nitrate, 4-nitrobenzimidazole and 2-ethyl-5-nitrobenzimidazole.

11. The silver halide photosensitive material as in claim 1 wherein said polymer containing greater than 50 mole percent of the recurring unit represented by the general formula (II) is a homopolymer selected from the group consisting of poly-N-vinyl-N-methylformamide, poly-N-vinyl-N-methylacetamide, poly-N-vinyl-N-methylpropionamide, poly-N-vinyl-N-ethylformamide, poly-N-vinyl-N-ethylacetamide, poly-N-vinyl-N-ethylpropionamide, poly-N-vinylpyrrolidone, poly-N-vinylpiperidone and poly-N-vinylcaprolactam.

12. The silver halide photosensitive material as in claim 1 in which the polymer containing greater than 50 mole percent of the recurring unit represented by the general formula (III) is selected from the group consisting of copolymers of N-vinylpyrrolidone with vinyl alcohol, N-vinylpyrrolidone with N-methylol acrylamide, N-vinylpyrrolidone with N-methylacrylamide, N-vinylpyrrolidone with acrylonitrile, N-vinyl-N-methylformamide with vinyl alcohol, N-vinyl-N-methylformamide with acrylic acid, N-vinyl-N-methylformamide with vinyl acetate, N-vinyl-N-methylformamide with acryloylmorpholine, N-vinyl-N-ethylformamide with vinyl alcohol, N-vinyl-N-ethylformamide with acrylamide, N-vinyl-N-ethylformamide with acrylonitrile and N-vinyl-N-ethylformamide with methacrylic acid.

13. The silver halide photosensitive material as in claim 1 in which any homopolymer or copolymer has a molecular weight of from about 4,000 to about 1,000,000.

14. The silver halide photosensitive material as in claim 13 where the molecular weight is from 5,000 to 500,000.

15. The silver halide photosensitive material as in claim 1 where the total amount of the compound of general formula (I) is from 0.5 to 100 mg. per mole of silver halide contained in the silver halide emulsion layer and the total amount of the polymer containing greater than 50 mole percent of the recurring unit represened by the general formula (II) is from 0.05 to 5 g. per mole of the silver halide contained in the silver halide emulsion layer.

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U.S. Cl. X.R.

96—109