United States Patent Office 3,393,072 Patented July 16, 1968

3,393,072

DIOXIMES AS ANTIFOGGANTS IN SILVER HALIDE EMULSIONS

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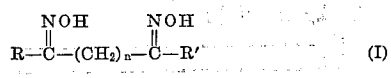
No Drawing. Filed Apr. 14, 1965, Ser. No. 447,986
Claims priority, application Japan, Apr. 23, 1964, 39/22,685
4 Claims. (Cl. 96—109)

This invention relates to photographic materials and more particularly to a method for preventing the formation of fog and black spots in photographic emulsion with dioxime compounds.

It has been well known that a photographic emulsion on storage tends to become spontaneously developable without exposure to light. There is normally a detectable amount of silver salts reduced during development in the areas where no exposure was given; this is commonly called fog. The formation of fog is promoted by bad conditions in storage as well as bad conditions in development. When a photographic material wetted by developing solution is exposed to air in development, the formation of fog is particularly promoted and we call it "airial fog" hereinafter. Moreover fog is also formed by the presence of fine iron particles or other fine impurity particles contained in supports, gelatin or chemicals. These impurity particles may also enter into photographic materials during the production or treatment of them. And in this case particularly spot-like fog having a high optical density, which is generally called "black spot" is usually formed.

For preventing the formation of such airial fog and black spots the additions of various compounds have been proposed, but their effects are usually weak and even though some of them are effective they give other bad influences, such as, reduction of sensitivity, deterioration of the quality of gelatin layers, etc.

We have found that the formation of airial fog and black spots can be remarkably suppressed by the addition of compounds shown by the following general Formula I.



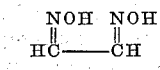
(I)

(Wherein R and R' each represents a hydrogen atom, a lower alkly group, an aryl group, a heterocyclic group containing an oxygen atom or a nitrogen atom, or a carboxyl group and *n* represents 0, 1 or 2.)

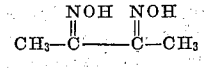
in an emulsion layer and/or a protective layer of silver halide photographic materials.

Representative compounds of the above mentioned general Formula I, which can be used in this invention, are as follows:

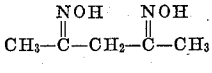
(1)



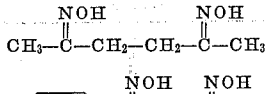
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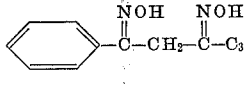
(3)



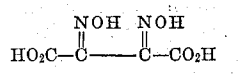
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(5)

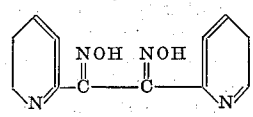


(6)

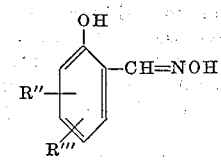


and

(7)



The compounds of this invention may be used individually or may be used as a mixture of two or more of these compounds. Further, in another embodiment of this invention the compound of the above general formula may be used with salicylaldoxime or its derivatives shown by the following general Formula II



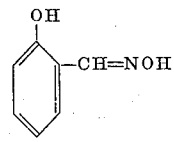
(II)

(Wherein R'' and R''' each represents a hydrogen atom, OH group, or a lower alkyl group.)

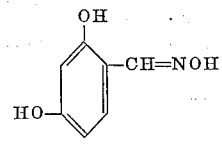
whereby the formation of airial fog and black spots can be more remarkably prevented.

Representative compounds of the general Formula II which can be used in this invention are as follows.

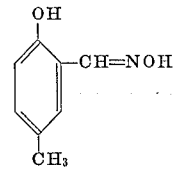
(8)



(9)

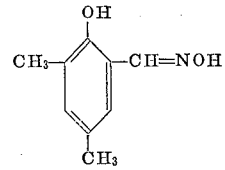


(10)



and

(11)



It has been already disclosed in B.P. 623,448 that a salicylaldoxime is used for preventing the formation of airial fog but when the salicylaldoxime is used with the compounds of this invention shown in general Formula I, it gives an excellent effect for preventing the formation of airial fog and black spots, which has never been attained by the use of the salicyladoxime alone.

The compound (I) and compound (II) may be added at any stage of the production of emulsions but it is preferable to add them after ripening and before coating. There are no limitations for the amount of them but the amount of compound (I) is suitably 3–50 g., and more

preferably 10–20 g. per 1 kg. of gelatin in a silver halide photographic emulsion layer or a protective coating layer. Further, when compound (II) is used together with compound (I), the amount of compound (II) is suitably 10–100 g. and more preferably 20–50 g. per 1 kg. of gelatin in a silver halide photographic emulsion layer or a protective coating layer.

A silver halide photographic emulsion that is used in this invention may be or may not be optically dye sensitized. Moreover, the silver halide photographic emulsion may be chemically sensitized with a sulfur-containing compound, a noble metal salt, a polyoxyethylene derivative, a polyamine, or a quaternary ammonium salt and also in order to improve the photographic characteristics it may contain a water-soluble polymer such as polyvinyl pyrrolidone. Further, in cases where a silver halide photographic emulsion contains a hardening agent, such as, formaline or mucochloric acid, a natural or synthetic surface active agent, and a stabilizer such as a tetraazindene compound, the addition of the dioxime compound of this invention in the emulsion can suppress effectively the formation of airial fog and black spots without reducing the desirable photographic properties of the photographic material endowed by the addition of these additives.

Example 1

A photographic sulfur sensitized, gold sensitized and optically cyanine dye sensitized high-speed panchromatic silver iodobromide emulsion for negative type photographic material, which contain 5 mole percent of silver iodide was dissolved by heating and added with fine particles of iron which had been prepared preliminary for promoting the formation of black spots caused artifically, The solution was divided into four equal volume portions after stirring for 10 minutes. Each of the divided solutions was added with above-stated compound (2) in the amount shown below and coated on a film base followed by drying. After developing for 10 minutes at 20° C., fixing, rinsing with water and drying, the sizes of formed black spots and the numbers of thus formed spots per 0.3 sq. m. were detected, which were shown below.

Amount of compound (2) (g./kg. gelatin)	No. of spots of 1–2 mm. diam.	No. of spots of 0.9–0.1 mm.	No. of spots below 0.09 mm.
0	3	4	62
3.5	2	1	41
7.0	0	0	28
10.5	0	0	13

No changes were observed in the photographic properties as well as the physical properties of the emulsion layers.

The composition of the used developing solution was as follows:

Warm water	cc.	500.0
Metol	g.	2.0
Sodium sulfite (anhydrous)	g.	100.0
Hydroquinone	g.	5.0
Borax	g.	20.0

Water to 1.0 liter.

Example 2

The high speed panchromatic silver iodobromide photographic emulsion in Example 1 was added with above described compound (3) in the amount shown below and set by cooling. On the emulsion were uniformly spread preliminary prepared fine particles of iron through a screen of 200 mesh and the emulsion was dried.

The thusly prepared photographic materials were developed for 10 minutes at 20° C. with the developing solution as in Example 1, and after fixing and rinsing with water, the relative density and sizes of formed black spots were detected, the results being as follows.

Amount of compd. (3) (g./kg.gelatin)	Size of spot (diam.-mm.)	Relative optical density of spot
0	2.4	4
3.5	1.5	3
7.0	1.1	2
10.5	0.8	1
14.0	0.9	1

When compound (5) was used instead of compound (3), almost the same results were obtained.

Example 3

A photographic sulfur sensitized and optically merocyanine dye sensitized high contrast orthochromatic silver bromochloride emulsion containing 30 mole percent of silver iodide was added with compound (2) in the amount shown below and coated on a film base then dried. For increasing airial fog artificially, the photographic material was developed as follows. That is, the photographic film was immersed in a developing solution for 1 minute at 20° C., exposed in air for 1 minute, and then immersed again in the developing solution for 1.5 minutes. After fixing, rinsing with water, and drying, the optical density of the formed airial fog is as follows:

Amount of compound (2), (g./kg. gelatin):	Optical density
0	1.5–2.0
7.0	0.15–0.20
14.0	0.05–0.06

The composition of the developing solution was as follows:

Warm water	ml.	500.0
Sodium sulfite (anhydrous)	g.	30.0
Paraformaldehyde	g.	7.5
Acid sodium sulfite	g.	2.2
Boric acid	g.	7.5
Hydroquinone	g.	22.5
Potassium bromide	g.	1.6
Water liters to		1.0

Example 4

A protective coating layer for the high-contrast orthochromatic silver chlorobromide photographic emulsion in Example 3 was added with above-mentioned compound (1) and treated as in Example 3. The results are shown below.

Amount of compd. (1) (g./kg. gelatin):	Optical density of air fogs
0	1.5–2.0
7.0	0.5–0.6
14.0	0.15–0.25
21.0	0.15–0.20
28.0	0.05–0.06

When above-shown compound (6) was used instead of using compound (1), almost the same results were obtained.

Example 5

A high-contrast orthochromatic sliver chlorobromide photographic emulsion containing 18 mole percent of silver bromide had been sensitized chemically with a sulfur-containing compound and a gold compound and optically with a merocyanine dye was added with above-shown compound (2) and compound (8) together in the amounts shown in the following table and coated on a film base followed by treating as in Example 3. The results are shown in the following table.

Amount of compd. (2) (g./kg. gelatin)	Amount of compd. (8) (g./kg. gelatin)	Optical density of air fog
0	0	2.0–2.5
3.5	0	0.20–0.25
7.0	0	0.15–0.20
14.0	0	0.15–0.20
0	30	0.20–0.25
0	45	0.15–0.20
7.0	30	0.05–0.08
14.0	30	0.05–0.06

When compounds (9), (10) and (11) were used respectively instead of compound (8), almost the same results were obtained.

Example 6

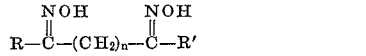
A photographic sulfur sensitized, gold sensitized and optically merocyanine dye sensitized high-contrast orthochromatic silver chlorobromide emulsion containing 18 mole percent of silver bromide was additionally sensitized with 95 mg. of the condensation product of nonylphenol with approximately 20 moles of ethylene oxide.

The emulsion was added with compound (1) and compound (9) in the amounts shown in the following table then coated on a film base, and followed by treating as in Example 3. The results are as follows:

Amount of compd. (1) (g./kg. gelatin)	Amount of compd. (9) (g./kg. gelatin)	Optical density of air fog
0	20	0.30–0.20
0	30	0.30–0.20
3.0	20	0.09–0.05
6.0	20	0.07–0.05

What we claim is:

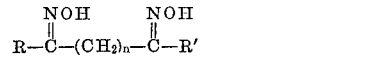
1. A silver halide photographic material comprising a support and a silver halide photographic emulsion layer, said emulsion layer containing at least one compound shown by the general Formula I



(I)

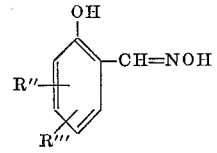
wherein R and R′ each represents a member selected from the class consisting of a hydrogen atom, a lower alkyl group, an aryl group, a heterocyclic group containing an oxygen atom, a heterocyclic group containing a nitrogen atom, and a carboxylic group and *n* represents 0, 1 and 2.

2. A silver halide photographic material comprising a support and a silver halide photographic emulsion layer, said emulsion layer containing at least a compound shown by the general Formula I



(I)

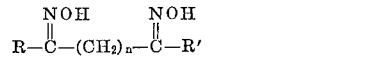
wherein R and R′ each represents a member selected from the class consisting of a hydrogen atom, a lower alkyl group, an aryl group, a heterocyclic group containing an oxygen atom, a heterocyclic group containing a nitrogen atom, and a carboxylic group and *n* represents 0, 1 and 2, and at least one compound shown by the following general Formula II



(II)

wherein R″ and R‴ each represents a member selected from the class consisting of a hydrogen atom, OH group, and a lower alkyl group.

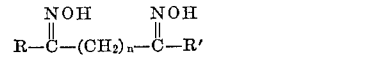
3. A silver halide photographic material comprising a support, a silver halide photographic emulsion layer, and a protective layer for the emulsion layer, at least one of said layers containing at least a compound shown by the general Formula I



(I)

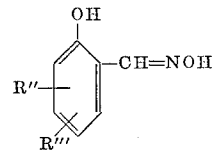
wherein R and R′ each represents a member selected from the class consisting of a hydrogen atom, a lower alkyl group, and aryl group, a heterocyclic group containing an oxygen atom, a heterocyclic group containing a nitrogen atom, and a carbocyclic group and *n* represents 0, 1 and 2.

4. A silver halide photographic sensitive material comprising a support, a silver halide photographic sensitive emulsion layer, and a protective layer for the emulsion layer, at least one of said layers containing at least a compound shown by the general Formula I



(I)

wherein R and R′ each represents a member selected from the class consisting of a hydrogen atom, a lower alkyl group, an aryl group, a heterocyclic group containing an oxygen atom, a heterocyclic group containing a nitrogen atom, and a carboxylic group and *n* represents 0, 1 and 2, and a compound shown by the following general Formula II



(II)

wherein R″ and R‴ each represents a member selected from the class consisting of a hydrogen atom, OH group, and a lower alkyl group.

References Cited

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533,034 11/1956 Canada.

NORMAN G. TORCHIN, *Primary Examiner.*

R. E. FICHTER, *Assistant Examiner.*