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[54] LIGHT-SENSITIVE SILVER HALIDE PHOTOGRAPHIC MATERIAL

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[52] **U.S. Cl.** .... **96/76 R;** 96/109; 96/66.5
[51] **Int. Cl.**^{2} **G03C 1/48;** G03C 1/34
[58] **Field of Search** .... 96/109, 76 R, 66.5

[56] **References Cited**

UNITED STATES PATENTS

3,679,424	7/1972	Barbier et al.	96/109

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Attorney, Agent, or Firm—Waters, Schwartz & Nissen

[57] ABSTRACT

This invention relates to stabilized, light-sensitive photographic material free of formation of fog comprising a fog-free silver halide emulsion and an inorganic or organic acid salt of nitron in the silver halide emulsion layer and/or a layer adjacent thereto, the amount of nitron being about 10 mg. to less than 100 mg. per mole of the silver halide.

1 Claim, No Drawings

LIGHT-SENSITIVE SILVER HALIDE PHOTOGRAPHIC MATERIAL

This invention relates to a stabilized light-sensitive silver halide photographic material free from formation of fog. More particularly, the invention is concerned with a light-sensitive silver halide photographic material which has successfully been prevented from formation of fog by incorporating an inorganic or organic acid salt of nitron into the silver halide emulsion layer and/or a layer adjacent thereto.

Generally, a light-sensitive silver halide photographic material tends to form, at the time of development, so-called chemical fog due to deposition of blackened silver even at portions which have not been exposed to light prior to development. The formation of fog is a fatal drawback of photographic material, since it greatly deteriorates the quality of the resulting photographic image.

With an aim to prevent light-sensitive silver halide photographic materials from formation of fog, there have heretofore been made many such attempts as, for example, to improve the equipments or vessels used for preparation of silver halide emulsions, to improve the prescriptions of silver halide emulsions, or to incorporate antifoggants such as tetrazaindene type or resorcinol type compounds into silver halide emulsions. However, it has been difficult to completely prevent silver halide photographic materials from formation of fog, and the actual state is such that the photographic materials are used while permitting the formation of fog to such an extent as to be practically bearable.

With recent demand for high speed silver halide photographic materials, there have come to be adopted such processing procedures that silver halide emulsions high in content of silver are coated in thin layers and further subjected to quick drying. In the case of silver halide photographic materials prepared by the above-mentioned processing procedures, fog of such an extent as to be practically bearable, which fog has heretofore been formed in the conventional photographic materials, is greatly enlarged and emphasized to cause a serious disadvantage. The formation of such fog is considered ascribable to the point that a physical impact is applied to silver halide particles due to a rapid shrinking phenomenon of protective colloids coating the silver halide particles. In order to alleviate the above-mentioned phenomenon, there have been made such attempts that softeners, e.g., water-soluble high molecular compounds such as polyacrylamide or polyvinyl alcohols, or wetting agents, e.g., aqueous dispersions of glycerin, hexylene glycol, polyethylene glycol, diethylene glycol polymer or vinyl polymer, are incorporated into the silver halide emulsion layers to physically inhibit the formation of fog. When said softeners or wetting agents are used, it is possible to prevent to a certain extent the formation of fog derived from thin layer-coating and quick drying of silver halide emulsions high in content of silver. However, since the softeners or wetting agents are still tacky even after drying of the silver halide emulsions, adhesion, peeling or transfer takes place between mutual silver halide photographic materials obtained, or between the photographic materials and insert papers, sensitizing papers or packing papers, with the result that the photographic materials, when developed, undesirably form white spots or black spots. Even in the case of silver halide photographic materials containing antifoggants, e.g., tetrazaindene type or resorcinol type compounds, and softeners or wetting agents, marked formation of fog is observed when they are stored under high temperature and humidity conditions or subjected to high temperature quick development. Thus, stabilized silver halide photographic materials capable of withstanding severe processing conditions, storage conditions and treatment conditions, which are required in recent years, have not actually be obtained yet.

An object of the present invention is to provide a stabilized light-sensitive silver halide photographic material free from formation of fog.

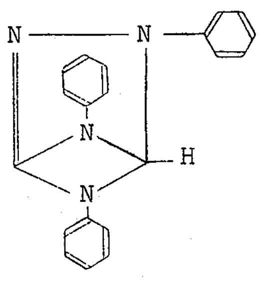
Another object of the invention is to provide a fog-free light-sensitive silver halide photographic material which is high in speed and can withstand severe processing conditions including such steps that a silver halide emulsion high in content of silver is coated in thin layer on a film base and is further subjected to quick drying.

A further object of the invention is to provide a stabilized light-sensitive silver halide photographic material which is prepared under such severe conditions as mentioned above but does not suffer from formation of fog even when stored under high temperature and humidity conditions or subjected to high temperature quick development.

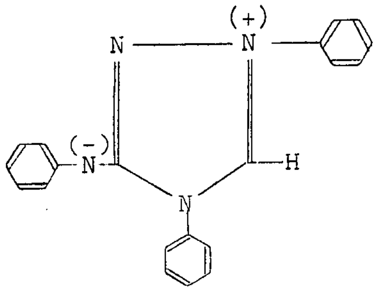
We have found that the above-mentioned objects can be accomplished by incorporating an inorganic or organic acid salt of nitron into the silver halide emulsion layer, and/or a layer adjacent thereto, of a light-sensitive silver halide photographic material. That is, even a light-sensitive silver halide photographic material prepared under severe conditions including steps, in which a silver halide emulsion high in speed and high in content of silver is coated in thin layer and is further subjected to quick drying, can be prevented from formation of fog, without being deteriorated in speed and contrast, by incorporating an inorganic or organic acid salt (hereinafter referred to as "nitron compound A") into the silver halide emulsion layer or a layer adjacent thereto. Further, even when the light-sensitive silver halide photographic material, which has been prepared under such severe conditions as mentioned above, is stored under high temperature and humidity conditions and subjected to high temperature quick treatment, stabilized photographic properties free from fog can be maintained.

While more or less antifogging effects can be observed even when the nitron compound A used in the present invention is replaced by nitron, the use of the nitron compound A results in unexpected antifogging effects.

The nitron compound A used in the present invention, which compound might include various compounds, is an inorganic or organic salt of, for example, the nitron compound of the structural formula (I) or (II),



(I)



(II)

which is disclosed in Journal of the Chemical Society, No. 1, pages 824–825 (1938). Concrete examples of the nitron compound A include hydrochloride, hydrobromide, nitrate, perchlorate, thiocyanate and acetate of nitron. Processes for preparing these nitron compounds A are described in Beilsteins Handbuch der Organischen Chemie, Vol. 26, page 349.

The nitron compound A according to the present invention is preferably incorporated into the silver halide emulsion layer of a light-sensitive silver halide photographic material, but may be incorporated into a sub layer, protective layer, inter layer or the like layer adjacent to the silver halide emulsion layer. When desired to be incorporated into the silver halide emulsion layer, the nitron compound A may be added to the silver halide emulsion at any stage before coating, but is preferably added at a stage from chemical ripening to coating. In this case, the nitron compound A may be added in the form of a solution in one or more of water and water-miscible solvents such as, for example, lower alcohols, esters and ketones.

The amount of the nitron compound A to be added varies depending on the kind of the silver halide emulsion or of the nitron compound A, but is ordinarily in the range of 1 mg. to 1,000 mg., preferably 10 mg. to 100 mg., per mole of the silver halide.

Silver halide emulsions applicable to the light-sensitive silver halide photographic materials of the present invention are black-white photographic emulsions, X-ray photographic emulsions, printing or copying photographic emulsions, internal or external color photographic emulsions, and diffusion transfer type black-white or color photographic emulsions, which may contain various silver halides such as silver bromide, silver iodobromide, silver chlorobromide and silver chloroiodobromide. These silver halide emulsions may have been sensitized with chemical sensitizers such as noble metal sensitizers, sulfur sensitizers or reduction sensitizers, or with color sensitizers, and may have been incorporated with conventional photographic additives such as hardeners, stabilizers and coating aids.

The thus constructed light-sensitive silver halide photographic materials of the present invention show stabilized photographic properties free from fog, even when prepared by use of silver halide emulsions high in speed and high in content of silver which have been coated in thin layers and subjected to quick drying. Further, even when the thus obtained photographic materials are stored under high temperature and humidity conditions or subjected to high temperature quick development, the stabilized photographic properties free from fog can be maintained.

The present invention is illustrated in detail below with reference to examples, but the scope of the invention is not limited to the examples.

EXAMPLE 1

A high speed silver iodobromide emulsion containing 1.5 mole% of silver iodide was subjected to second ripening according to gold sensitization and sulfur sensitization. Thereafter, the emulsion was incorporated with 4.0 g. per mole of the silver halide of 4-hydroxy-6-methyl-1,3,3*a*-7-tetrazaindene as a stabilizer, and with appropriate amounts of a coating aid and a hardener. The thus treated silver halide emulsion was equally divided into 7 portions. One of the 7 portions was coated in multi-layers on a polyethylene terephthalate film base with simultaneous application of a protective layer-forming 2.5% aqueous gelatin solution, and the resulting photosensitive film was quickly dried in 10 minutes in an atmosphere of 30°C. and RH 40% to prepare a control sample (Sample No. 1). Separately, the remaining 6 portions were individually treated in the same manner as in the case of the control sample, except that nitron or an inorganic acid salt of nitron was added, to prepare samples (Sample Nos. 2, 3, 4, 5 and 6).

The control sample and the samples were individually exposed to white light according to JIS by use of Sensitometer Model KS-1 (manufactured by Konishiroku Photo Industry Co., Ltd.), and then subjected to high temperature quick development at 40°C. for 30 seconds by means of a continuous roller type automatic developing machine capable of conducting the development, fixing, water-washing and drying of photographic materials successively, using a developer of the following composition:

Anhydrous sodium sulfite	70	g.
Hydroquinone	10	g.
Anhydrous boric acid	1	g.
Sodium carbonate (monohydrate)	20	g.
1-Phenyl-1,3-pyrazolidone	0.35	g.
Sodium hydroxide	5	g.
5-Methylbenzotriazole	0.05	g.
Potassium bromide	5	g.
Glutaraldehyde bisulfite	15	g.
Glacial acetic acid	8	g.
Water to make	1	liter

The thus treated samples were subjected to sensitometry to measure the photographic properties thereof. The results obtained were as set forth in Table 1. In Table 1, "Speed" shows a relative value calculated by assuming as 100 the speed of the control sample (Sample No. 1) containing no nitron compound A.

Table 1

Sample No.	Kind and amount (mg/mole silver halide) of nitron compound A		Photographic properties Speed	Fog	Gamma
1	—		100	0.27	1.11
2	Nitron	40	110	0.17	1.11
3	Nitron	60	105	0.16	1.12
4	Nitron hydrobromide	40	115	0.11	1.20
5	Nitron hydrobromide	60	100	0.10	1.14
6	Nitron hydrochloride	40	120	0.12	1.18
7	Nitron hydrochloride	60	110	0.11	1.16

From Table 1, it will be understood that when incorporated with nitron hydrobromide or hydrochloride according to the present invention, even a high speed silver halide photographic material, which was subjected to low humidity quick drying and to high temperature quick development, can display excellent photographic properties free from fog and high in gradation without deterioration in speed.

EXAMPLE 2

An X-ray silver iodobromide emulsion containing 2 mole% of silver iodide was subjected to second ripening and sensitized to the maximum speed by addition of gold and sulfur sensitizers. Thereafter, the emulsion was incorporated with 4.0 g. per mole of the silver halide of 4-hydroxy-6-methyl-1,3,3*a*-7-tetrazaindene as a stabilizer, and with appropriate amounts of a coating aid and a hardener. The thus treated silver halide emulsion was equally divided into 11 portions. One of the 11 portions was coated in multi-layers on a polyethylene terephthalate film base together with simultaneous application of a protective layer-forming 2.5% aqueous gelatin solution, and the resulting photosensitive film was quickly dried in the same manner as in Example 1 to prepare a control sample (Sample No. 8). Separately, the remaining 10 portions were individually treated in the same manner as in the case of the control sample, except that a nitron compound A was added in such proportion as shown in Table 2, to prepare 10 samples (Sample Nos. 9, 10, 11, 12, 13, 14, 15, 16, 17 and 18).

The control sample and the samples were individually exposed for 0.5 seconds to X-rays at a voltage of 60 KV and a current of 200 mA, through a fluorescent, medical X-ray screen having a medium sensitivity (KYOKKO. FS, emission spectrum maximum 4250A; manufactured by Dainippon Paint Co., Ltd.) and through an aluminum-made $\sqrt{2}$ step wedge. Subsequently, the samples were subjected to the same development, fixing, water-washing and sensitometry as in Example 1. Photographic properties of the samples were as set forth in Table 2. In Table 2, "Speed" shows a relative value calculated by assuming as 100 the speed of the control sample (Sample No. 8) containing no nitron compound A.

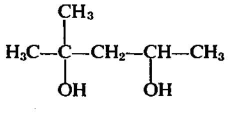
Table 2

Sample No.	Kind and amount (mg/mole silver halide) of nitron compound A		Photographic properties Speed	Fog
8	—		100	0.30
9	Nitron hydrobromide	10	100	0.21
10	Nitron hydrobromide	20	110	0.17
11	Nitron hydrobromide	30	117	0.14
12	Nitron hydrobromide	40	120	0.11
13	Nitron hydrobromide	60	118	0.10
14	Nitron acetate	10	100	0.21
15	Nitron acetate	20	105	0.18
16	Nitron acetate	30	115	0.15
17	Nitron acetate	40	118	0.12
18	Nitron acetate	60	118	0.11

From Table 2, it will be understood that when incorporated with nitron hydrobromide or acetate according to the present invention, even a high speed X-ray silver halide photographic material, which was subjected to severe drying and to high temperature quick development, is high in speed and gives a clear X-ray image free from fog.

EXAMPLE 3

The same treated silver halide emulsion as in Example 1 was equally divided into 2 portions. One of the 2 portions was coated in multi-layers on a polyethylene terephthalate film base together with the simultaneous application of a protective layer-forming 2.5% aqueous gelatin solution, and the resulting photosensitive film was quickly dried in 10 minutes in a low humidity atmosphere of 30°C. and RH 37% to prepare a control sample (Sample No. 19). Separately, the other portion was incorporated with 10 g. per mole of the silver halide of, as a control compound, the compound of the structure,



$$H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{C}}-CH_2-\underset{\displaystyle OH}{CH}-CH_3$$

which is disclosed in U.S. Pat. No. 2,960,404. This emulsion was equally divided into 4 portions. One of the 4 portions was treated in the same manner as in the case of the control sample (Sample No. 19) to prepare another control sample (Sample No. 20). The remaining 3 portions were individually treated in the same manner as in the case of the control sample (Sample No. 20), except that 45 mg. per mole of the silver halide of a nitron compound A was added, to prepare samples (Sample Nos. 21, 22 and 23).

The control samples and the samples were individually subjected to storage test and then subjected to the same development, fixing, water-washing and sensitometry as in Example 1. Photographic properties of the samples were as set forth in Table 3.

Table 3

Sample No.	Nitron compound A used	Photographic properties (Storage test) Incubated for 3 days at 20°C and 60% RH Speed	Fog	Gamma	Incubated for 3 days at 50°C and 80% RH Speed	Fog	Gamma
19	—	100	0.29	1.11	96	0.36	1.08
20	—	105	0.16	1.13	100	0.27	1.12
21	Nitron perchlorate	110	0.11	1.11	105	0.12	1.11
22	Nitron hydrobromide	115	0.12	1.12	115	0.11	1.12
23	Nitron acetate	110	0.11	1.12	110	0.11	1.11

From Table 3, it will be understood that when incorporated with nitron perchlorate, hydrobromide or acetate according to the present invention, even a silver halide photographic material, which was subjected to quick drying, high temperature quick development and storage under high humidity conditions, can display excellent photographic properties free from fog without degradation in speed.

EXAMPLE 4

The same treated silver halide emulsion as in Example 1 was equally divided into 2 portions. One of the 2 portions was coated in multi-layers on a polyethylene terephthalate film base with simultaneous application of a protective layer-forming 2% aqueous gelatin solution, and the resulting photosensitive film was quickly dried in an atmosphere of 30°C. and RH 37%. Separately, the other portion was treated in the same manner as in the case of the control sample, except that the protective layer-forming gelatin solution was incorporated with 5 mg. per g. of the gelatin of nitron hydrobromide, to prepare a sample.

The control sample and the sample were individually subjected to the same development and sensitometry as in Example 1, and compared in photographic properties. As the result, the sample was less in fog and clearer in image than the control sample, and showed no deterioration in speed at all.

What we claim is:

1. A stabilized, light-sensitive photographic material free of formation of fog comprising a fog-free silver halide emulsion and an inorganic or organic acid salt of nitron in the silver halide emulsion layer and/or a layer adjacent thereto, the amount of nitron being about 10 mg. to less than 100 mg. per mole of the silver halide.

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