# United States Patent

[11] 3,615,619

[72] Inventors **Toshihiko Yamamoto**
**Tokyo;**
**Kazuo Matui, Tokyo; Sadao Sugita, Hanno, all of Japan**

[21] Appl. No. **23,998**
[22] Filed **Mar. 30, 1970**
[45] Patented **Oct. 26, 1971**

[73] Assignee **Konishiroku Photo Industry Co., Ltd.**
**Tokyo, Japan**

[32] Priority **Mar. 25, 1969**
[33] **Japan**
[31] **44/22051**

---

[54] **PHENANTHROLINE ANTIFOGGANTS FOR SILVER HALIDE EMULSIONS**
**4 Claims, No Drawings**

[52] **U.S. Cl.** ..... **96/109,** 96/100
[51] **Int. Cl.** ..... **G03c 1/34**
[50] **Field of Search** ..... 96/109, 100, 66.5

[56] **References Cited**

UNITED STATES PATENTS

| | | | |
|---|---|---|---|
| 3,220,935 | 11/1965 | Nations et al. ..... | 203/6 |

FOREIGN PATENTS

| | | | |
|---|---|---|---|
| 587,481 | 4/1947 | Great Britain ..... | 96/106 |

*Primary Examiner*—Norman G. Torchin
*Assistant Examiner*—Won H. Louie, Jr.
*Attorney*—Waters, Roditi, Schwartz & Nissen

---

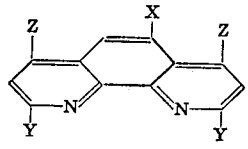
**ABSTRACT:** A photographic material comprising phenanthroline antifogging agents for silver halide emulsions.

# PHENANTHROLINE ANTIFOGGANTS FOR SILVER HALIDE EMULSIONS

This invention relates to a light-sensitive silver halide photographic material characterized in that a certain phenanthroline has been incorporated as an antifoggant into at least one of the layers constituting the photographic material.

Generally, a light-sensitive silver halide photographic material tends to form fog when treated with a developer at a relatively high temperature. It is well known that such fog formation is ascribable to the fact that the activation energy of development of fog is greater than that of development of image at a high temperature. Accordingly, the development of photographic material at elevated temperatures should be avoided as far as possible. In practice, however, there are many cases where the adoption of a relatively high temperature is inevitable owing to weather conditions or the adoption of a particularly high developer temperature is necessary in carrying out rapid development. For these reasons, there has been desired the production of light-sensitive photographic materials which are less in fog and stain even when developed at elevated temperatures. Hitherto, however, no light-sensitive photographic material satisfying the said desire has yet been obtained.

With an aim to satisfy the above-mentioned desire, the present inventors made extensive studies to find that when a phenanthroline represented by the formula



wherein *X* is a hydrogen or halogen atom, or an alkyl or aryl group or a group derived therefrom; *Z* is a hydrogen atom, or an alkyl or aryl group or a group derived therefrom; and *Y* is a hydrogen atom, or an alkyl or alkoxy group or a group derived therefrom, is incorporated into at least one of the emulsion layer, sublayer, interlayer, protective layer and backing layer constituting a light-sensitive silver halide photographic material, the photographic material is not only greatly decreased in formation of fog and in formation of color fog and stain in color photography which are brought about due to high-temperature development, but also is enhanced in storability.

Typical examples of the compounds represented by the above-mentioned formula which are used in the present invention are as shown in the table below, but it is needless to say that compounds usable in the present invention are not limited only to these compounds.



These compounds may be effectively incorporated into any layers constituting light-sensitive materials, but are most preferably incorporated into photographic emulsions which have completed second ripening. Alternatively, however, they may also be incorporated into photographic emulsions before or during second ripening thereby to prevent the formation of fogged nucleus. Further, the compounds may be applied to so-called protect-type color photographic emulsions by mixing them with water-insoluble or difficultly water-soluble couplers, dissolving the mixtures in water-immiscible high-boiling solvents and then dispersing the solutions in the photographic emulsions.

The amounts of the compounds to be incorporated vary depending on the kind of the emulsions, the kind of the compounds, the conditions of desired fog inhibition, etc. Generally, however, they are used in amounts of **10** mg. to **1.0** g. per liter of the silver halide emulsions and are incorporated in the form of solutions in a suitable organic solvent such as, for example, methanol, ethanol, acetone, ethyl acetate or the like.

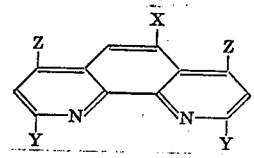
In case the compound is desired to be incorporated into auxiliary layers other than the emulsion layer, the amount of the compound is so controlled, in principle, that after preparation of light-sensitive material, the total amount of the compound per unit area becomes an amount within the above-mentioned range.

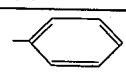
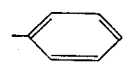
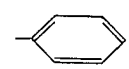
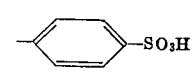
In embodying the present invention, the photographic emulsions may have been subjected to gold sensitization, sulfur sensitization and the like chemical sensitization or to spectral sensitization and the like. The compounds employed in the present invention can inhibit the formation of fog, which is liable to be formed due to said sensitization.

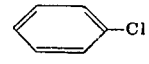
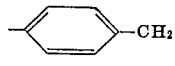
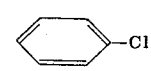
The present invention is illustrated in further detail below with reference to examples.

## EXAMPLE 1

A high-speed silver iodobromide emulsion for X-ray films was subjected to ordinary chemical ripening. To this emulsion were added 50 mg. per 100 cc. **of the emulsion of** 5-methyl-7-hydroxy-S-triazolo (2,3-*a*) pyrimidine as a stabilizer and 1 g. of saponin as a coating aid. The thus-treated emulsion was divided into 9 portions, and the 8 portions were individually incorporated with each of the compounds set forth in the table below, while the remaining 1 portion was left unincorporated. These emulsions were individually coated on a triacetate film base, followed by drying to prepare photographic films. Each of the thus prepared films was exposed according to the procedure described in JIS K-7609, was developed at 30°C C.



| Compound | (I) | (II) | (III) | (IV) | (V) | (VI) | (VII) | (VIII) |
|---|---|---|---|---|---|---|---|---|
| X | H | $NO_2$ | Cl | $CH_3$ |  | H | H | H |
| Z | H | H | H | H | H |  |  |  |
| Y | H | H | H | H | H | H | $CH_3$ | H |

| Compound | (IX) | (X) | (XI) | (XII) | (XIII) | (XIV) | (XV) |
|---|---|---|---|---|---|---|---|
| X | H | $-CH_3$ | $-t-C_4H_9$ | H |  | Br | $-C_3H_7$ |
| Z |  |  | H | H | H | $-CH_3$ |  |
| Y | $-CH_3$ | H | $-CH_3$ | $-OCH_3$ | $-OC_2H_4$ | $-CH_3$ | $-OCH_3$ |

The phenanthroline compounds represented by the above-mentioned formula are available in market as metal-chelating agents and colorimetric reagents.

for 1 minute and 30 seconds, at 35°C. for 40 seconds and at 40°C. for 25 seconds with a strongly alkaline PQ developer containing 1-phenyl-3-pyrazolidone-hydroquinone and was

then subjected to measurements of speed and fog to obtain the results shown in the following table:

| Compound incorporated | Amount incorporated per liter of emulsion (mg.) | 30° C., 1.5 min. | | 35° C., 40 sec. | | 40° C., 25 sec. | |
|---|---|---|---|---|---|---|---|
| | | Relative speed | Fog | Relative speed | Fog | Relative speed | Fog |
| None | | 100 | 0.20 | 100 | 0.42 | 100 | 0.76 |
| Exemplified compound (II) | 180 | 100 | 0.08 | 100 | 0.12 | 100 | 0.18 |
| Exemplified compound (IV) | 230 | 95 | 0.07 | 95 | 0.12 | 93 | 0.17 |
| Exemplified compound (V) | 260 | 100 | 0.06 | 100 | 0.10 | 95 | 0.13 |
| Exemplified compound (VI) | 220 | 100 | 0.03 | 100 | 0.05 | 100 | 0.10 |
| Exemplified compound (VII) | 250 | 95 | 0.05 | 95 | 0.06 | 90 | 0.08 |
| Exemplified compound (IX) | 310 | 100 | 0.12 | 90 | 0.18 | 90 | 0.23 |
| Exemplified compound (X) | 350 | 100 | 0.07 | 90 | 0.10 | 87 | 0.16 |
| Exemplified compound (XII) | 280 | 100 | 0.09 | 100 | 0.12 | 100 | 0.21 |

As is clear from the above table, the photographic materials incorporated with the compounds used in the present invention are inhibited in formation of fog owing to development without any detrimental effect on speed.

## EXAMPLE 2

To a green-sensitive high-speed silver iodobromide color photographic emulsion were added 20 mg. per 100 cc. of the emulsion of 5-methyl-7-hydroxy-S-triazolo (2,3-*a*) pyrimidine as a stabilizer and a solution in IN-caustic soda of 15 g. of a magenta coupler 1-(4-carboxyphenyl)-3-(4-palmitoylaminobenzoylamino)5-pyrazolone, and the thus treated emulsion was adjusted to pH 6.8 by addition of citric acid. This emulsion was divided in the same manner as in example 1, and the divided emulsions were individually incorporated with each of the compounds set forth in the table below and then coated on a film base, followed by drying to prepare color photographic films. Each of the thus prepared films was developed at 23°C. for 9 minutes and at 25°C. for 6 minutes with a color developer containing diethyl-p-phenylenediamine, and then subjected to water-washing, bleaching, water-washing, fixing, water-washing and drying in this order. Thereafter the measurements of speed and fog were effected to obtain the results as shown in the following table:

| Compound incorporated | Amount incorporated per liter of emulsion (mg.) | 23° C., 9 min. | | 25° C., 6 min. | |
|---|---|---|---|---|---|
| | | Relative speed | Developed fog density | Relative speed | Developed fog density |
| None | | 100 | 0.10 | 100 | 0.16 |
| Exemplified compound (I) | 120 | 105 | 0.02 | 100 | 0.05 |
| Exemplified compound (II) | 120 | 100 | 0.02 | 95 | 0.07 |
| Exemplified compound (VI) | 120 | 95 | 0.03 | 90 | 0.06 |
| Exemplified compound (VIII) | 120 | 100 | 0.02 | 100 | 0.04 |
| Exemplified compound (IX) | 120 | 100 | 0.03 | 95 | 0.07 |
| Exemplified compound (XI) | 120 | 100 | 0.03 | 90 | 0.05 |
| Exemplified compound (XIV) | 120 | 90 | 0.02 | 95 | 0.05 |

As is clear from the above table, the light-sensitive photographic materials in accordance with the present invention successfully inhibit the color fog formed at the time of color development.

## EXAMPLE 3

To a red-sensitive low-speed silver chlorobromide color photographic emulsion containing 25 mole percent of silver bromide were added 100 mg. per liter of the emulsion of 5-methyl-7-hydroxy-S-triazolo (2,3-*a*) pyrimidine as a stabilizer and a solution in IN-caustic soda of 20 g. of a cyan coupler 1-oxy-4-sulfo-2-naphthoic octadecylamide, and the thus treated emulsion was adjusted to pH 6.5 by addition of citric acid. The emulsion was divided into eight portions, and the seven portions were individually incorporated with each of the compounds set forth in the table below, while the remaining one portion was left unincorporated. These emulsions were individually coated on a photographic raw paper, followed by drying to prepare color photographic printing papers. Each of the thus prepared printing papers was developed at 28°C. for 4 minutes with a color developer containing p-aminoethylhydroxyethylaniline, was subjected to fixing, water-washing, bleaching, fixing, water-washing and drying in this order and was then measured in speed and fog to obtain the results shown in the following table:

| Compound incorporated | Amount incorporated per liter of emulsion (mg.) | Relative speed | Developed fog density |
|---|---|---|---|
| None | | 100 | 0.08 |
| Exemplified compound (I) | 100 | 90 | 0.03 |
| Exemplified compound (II) | 100 | 90 | 0.03 |
| Exemplified compound (III) | 100 | 90 | 0.04 |
| Exemplified compound (IV) | 100 | 95 | 0.03 |
| Exemplified compound (VIII) | 100 | 95 | 0.03 |
| Exemplified compound (XI) | 100 | 90 | 0.03 |
| Exemplified compound (XV) | 100 | 95 | 0.03 |

As is apparent also from the above table, the light-sensitive materials incorporated with the compounds employed in the present invention inhibit the color fog formed at the time of color development without any detrimental effects on speed.

## EXAMPLE 4

Each of the exemplified compounds (I), (IV), (VIII) and (XIV) was formed into a 2 percent methanol solution and was incorporated in such amount as shown in the table below into a 3 percent aqueous gelatine solution. To this solution was further added 20 cc. of a 5 percent saponin solution as a coating aid, and the resulting mixed solution was applied as a protective layer to a high-speed X-ray film and was then dried. The thus obtained photographic films and a photographic film prepared without use of any such compound as mentioned above were subjected to high-temperature development in the

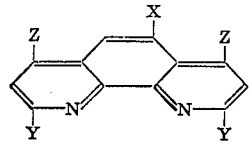
entirely same manner as in example 1 and were then measured in speed and fog to obtain the results as set forth in the following table:

| Compound incorporated | Amount incorporated per liter of 3% gelatine (mg.) | 30° C., 1.5 min. | | 35° C., 40 sec. | | 40° C., 25 sec. | |
|---|---|---|---|---|---|---|---|
| | | Relative speed | Fog | Relative speed | Fog | Relative speed | Fog |
| None | | 100 | 0.18 | 100 | 0.28 | 100 | 0.56 |
| Exemplified compound (I) | 200 | 105 | 0.06 | 100 | 0.10 | 105 | 0.18 |
| Exemplified compound (IV) | 240 | 95 | 0.08 | 100 | 0.12 | 100 | 0.22 |
| Exemplified compound (VIII) | 250 | 110 | 0.08 | 105 | 0.18 | 110 | 0.27 |
| Exemplified compound (XIV) | 200 | 95 | 0.05 | 100 | 0.07 | 110 | 0.10 |

As is clear from the above table, the photographic films in accordance with the present invention, which contain the above-mentioned phenanthroline compounds in the protective layers, successfully inhibit the formation of fog due to high-temperature development and show excellent photographic properties without degradation in speed.

What we claim is

1. A light-sensitive silver halide photographic material containing in at least one of the layers constituting the photographic material, a phenanthroline represented by the general formula




wherein $X$ is a hydrogen or halogen atom, or an alkyl or aryl group or a group derived therefrom; $Z$ is a hydrogen atom, or an alkyl or aryl group or a group derived therefrom; and $Y$ is a hydrogen atom, or an alkyl or alkoxy group or a group derived therefrom.

2. A light-sensitive silver halide photographic material as claimed in claim 1, wherein said phenanthroline is in at least one layer selected from the emulsion layer, sublayer, interlayer, protective layer and backing layer.

3. A light-sensitive silver halide photographic material as claimed in claim 1, wherein said phenanthroline is incorporated together with a color coupler into one or more emulsion layer to constitute a light-sensitive silver halide color-photographic material.

4. A light-sensitive silver halide photographic material as claimed in claim 1, wherein the amount of said phenanthroline contained is 10 mg. to 1.0 g. per liter of the silver halide emulsion used.

* * * * *