July 6, 1948. N. HEIMBACH ET AL 2,444,609

STABILIZERS FOR PHOTOGRAPHIC SILVER-HALIDE EMULSIONS

Filed May 18, 1946

FIG. 1.

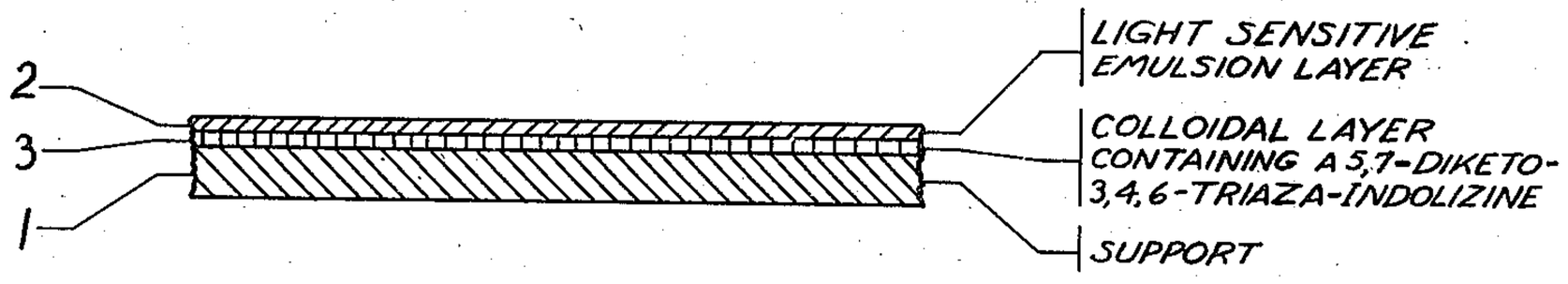


FIG. 2.

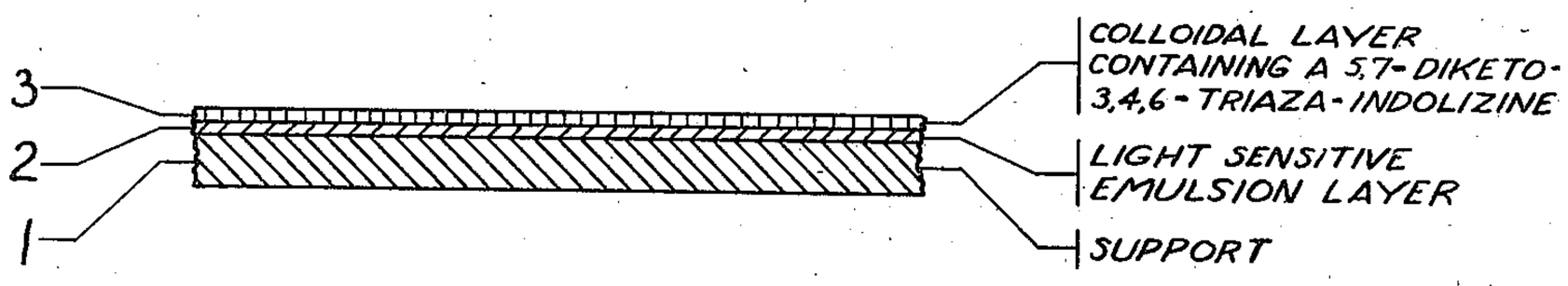


FIG. 3.

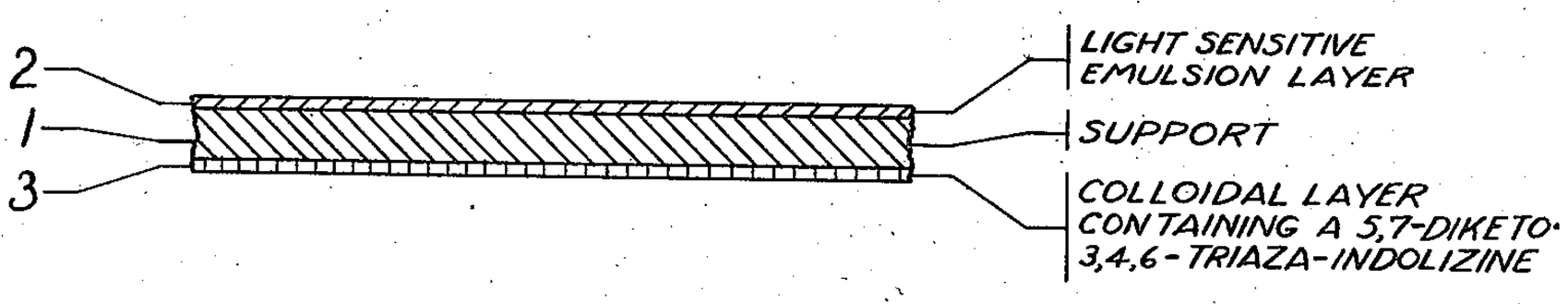
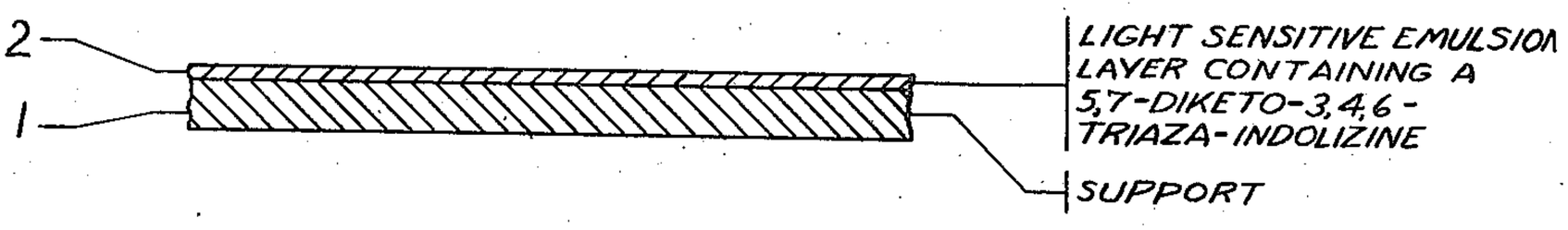


FIG. 4.



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UNITED STATES PATENT OFFICE

2,444,609

STABILIZERS FOR PHOTOGRAPHIC SILVER-HALIDE EMULSIONS

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Application May 18, 1946, Serial No. 670,687

11 Claims. (Cl. 95—7)

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This invention relates to the stabilization of light-sensitive silver-halide emulsions, and more particularly to the use of 5,7-diketo-3,4,6-triaza-indolizines as stabilizers.

It is known in the art that light-sensitive emulsions, such as gelatin silver-halide emulsions, have a decided tendency to fog. The fog may be of two types, namely, yellow fog and chemical (gray) fog. The yellow fog, sometimes referred to as color fog or dichroic fog, is essentially a colloidal deposit of silver, the color intensity and general appearance of which are determined by the minute particle size and degree of subdivision. The fog is chiefly yellow in color and is most apparent in the lighter portions of a negative. The color may vary, however, and the colloidal silver particles may, for example, appear green by reflected light and yellow or red by transmitted light. The so-called chemical fog, or gray fog, on the other hand, is the more common and is formed in a number of ways. It may be caused by premature exposure, by excessive ripening of the emulsion, or by the storage of the film, particularly at high temperatures or for unusually long periods of time.

The primary object of the present invention is to provide stabilizers or fog inhibiting agents which tend to prevent the formation of chemical fog, in light-sensitive silver-halide emulsions.

A further object is to provide stabilizers or anti-fogging agents for light-sensitive silver-halide emulsions, which do not lower the sensitivity of the emulsion, and which increase its stability.

Still further objects and advantages will appear from the following specification.

We have found that the above objects are accomplished by utilizing 5,7-diketo-3,4,6-triaza-

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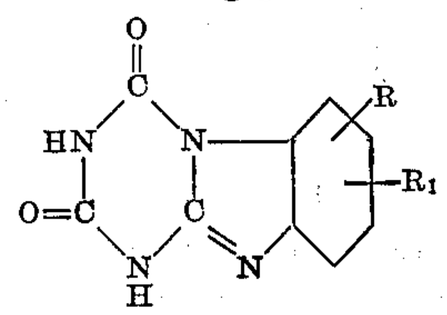
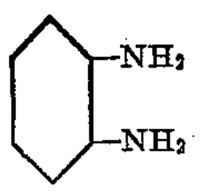
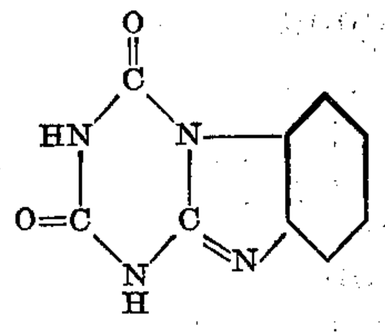
indolizines characterized by a structure corresponding to the following general formula:

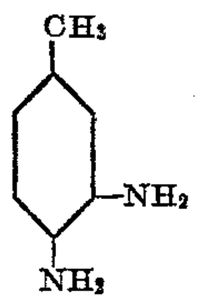
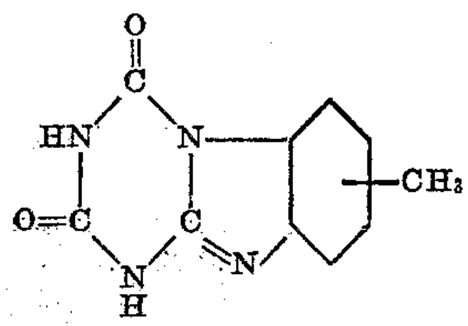
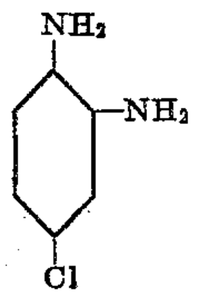
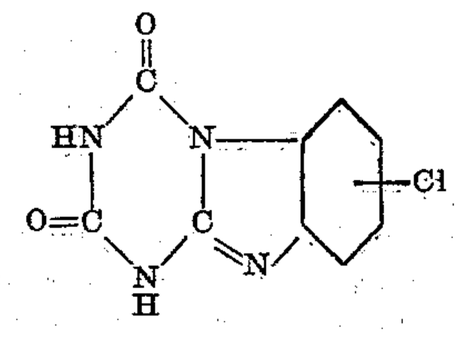
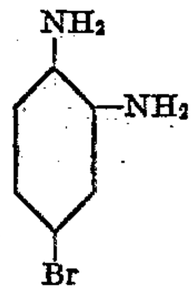
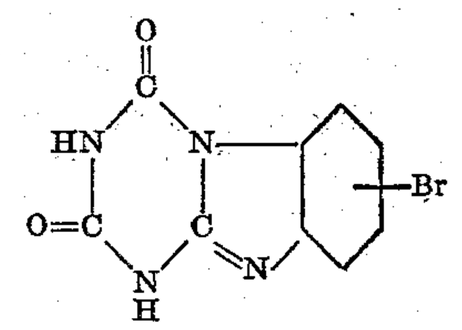
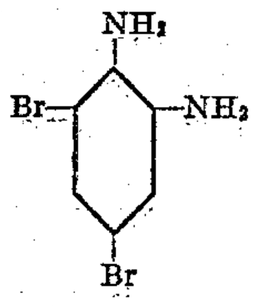
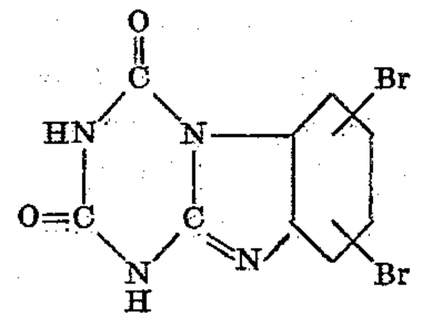
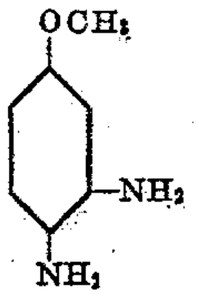
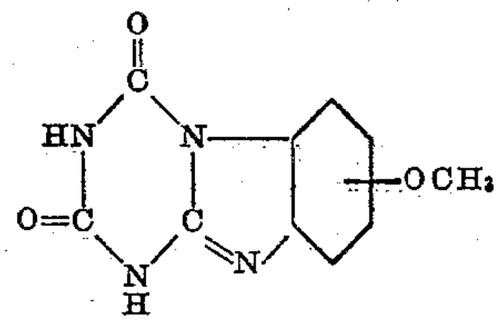
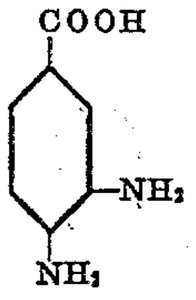
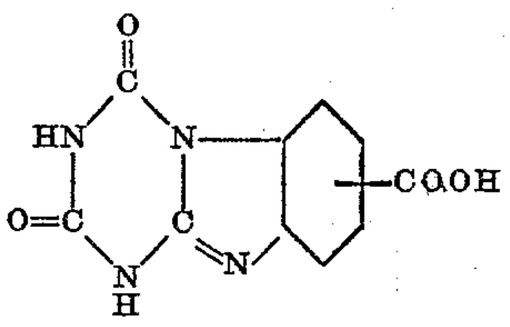


wherein R may be hydrogen or halogen, e. g., chlorine or bromine, and R_1 may be hydrogen, aliphatic, such as alkyl, e. g., methyl, ethyl, propyl, butyl, amyl, and the like, alkoxy, e. g., methoxy, ethoxy, propoxy, butoxy, etc., carbalkoxy, e. g., carbomethoxy, carbethoxy, carbopropoxy, etc., carboxy, or halogen of the same value as R.

It should be noted that the usefulness of the compounds represented by the above general formula is not dependent upon the nature of the phenyl ring so long as the phenyl ring, whether it be substituted or disubstituted, is a part of the indolizine nucleus.

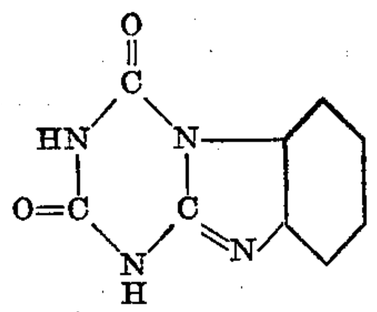
The method for the preparation of the 5,7-diketo-3,4,6-triaza-indolizines is given in Beilstein, 26, page 497. The method employed consists of reacting 1 mol of an o-phenylenediamine with 3 mols of cyanogen bromide in the presence of 4 mols of sodium or potassium bicarbonate. Since it is impossible to determine the exact course of the reaction with respect to the two amino groups of the o-phenylenediamine, the specific location of the phenyl substituents in the resulting indolizine cannot be ascertained with reasonable accuracy. Accordingly, therefore, it was deemed desirable, for the sake of clarity, to resort to the prefix "x" in naming the phenyl substituents in the examples. For the same reason, it was deemed advisable to list the following specific indolizines prepared according to the above procedure with the corresponding o-phenylenediamines from which they were obtained.

o-Phenylenediamines	Indolizines
I	
 o-Phenylenediamine	 5,7-diketo-4,5,6,7-tetrahydro-3,4,6-triaza-1,2-benzo-indolizine

o-Phenylenediamines	Indolizines
II	
 3,4-diaminotoluene	 5,7-diketo-4,5,6,7-tetrahydro-3,4,6-triaza-1,2-(*x*-methylbenzo)-indolizine
III	
 1,2-diamino-4-chlorobenzene	 5,7-diketo-4,5,6,7-tetrahydro-3,4,6-triaza-1,2-(*x*-chlorobenzo)-indolizine
IV	
 1,2-diamino-4-bromobenzene	 5,7-diketo-4,5,6,7-tetrahydro-3,4,6-triaza-1,2-(*x*-bromobenzo)-indolizine
V	
 1,2-diamino-4,6-dibromobenzene	 5,7-diketo-4,5,6,7-tetrahydro-3,4,6-triaza-1,2-(*xx*-dibromobenzo)-indolizine
VI	
 3,4-diaminoanisole	 5,7-diketo-4,5,6,7-tetrahydro-3,4,6-triaza-1,2-(*x*-methoxybenzo)-indolizine
VII	
 3,4-diaminobenzoic acid	 5,7-diketo-4,5,6,7-tetrahydro-3,4,6-triaza-1,2-(*x*-carboxybenzo)-indolizine

The following examples will serve to illustrate certain ways in which the stabilizers of our invention have been prepared and applied, but are not to be construed as limiting the invention.

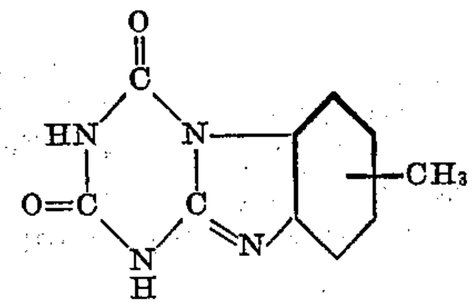
Example I



5,7-diketo-4,5,6,7-tetrahydro-3,4,6-triaza-1,2-benzo-indolizine

Seven grams of o-phenylenediamine were dissolved in 200 cc. of 50% ethyl alcohol to which was added 28 grams of potassium bicarbonate dissolved in 150 cc. of water. To this solution were added 22.5 grams of cyanogen bromide dissolved in 50 cc. of 95% ethyl alcohol with rapid stirring. The temperature rose slowly to 50–60° C., and the crude product precipitated shortly after the addition. The final product was recrystallized from glacial acetic acid as colorless microscopic prisms which did not melt below 320° C.

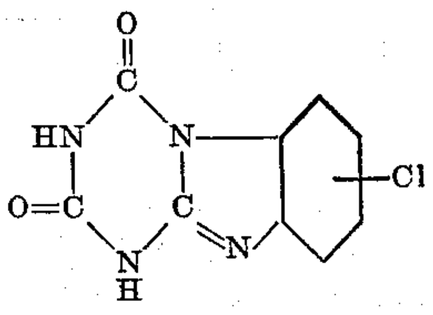
Example II



5,7-diketo-4,5,6,7-tetrahydro-3,4,6-triaza-1,2-(*x*-methylbenzo)-indolizine

Eight grams of 3,4-diaminotoluene were dissolved in 200 cc. of 50% ethyl alcohol to which were added 28 grams of potassium bicarbonate dissolved in 150 cc. of water. To this solution were added 22.5 grams of cyanogen bromide dissolved in 50 cc. of 95% ethyl alcohol with rapid stirring. The temperature rose slowly to 50–60° C. after this addition with the formation of a precipitate. The final product was crystallized from glacial acetic acid as colorless microscopic prisms which did not melt below 320° C.

Example III



5,7-diketo-4,5,6,7-tetrahydro-3,4,6-triaza-1,2-(*x*-chlorobenzo)-indolizine

Nine and three-tenths grams of 1,2-diamino-4-chlorobenzene were dissolved in 200 cc. of 75% ethyl alcohol. To this solution were added a solution of 22.5 grams of cyanogen bromide in 50 cc. of ethyl alcohol, followed by 28 grams of potassium bicarbonate dissolved in 150 cc. of water. The mixture was stirred continuously. A precipitate was gradually formed and the reaction appeared to be complete in one hour. The precipitate was purified by dissolving it in 10% sodium hydroxide solution, digested for 10 minutes with charcoal, filtered, and reprecipitated with dilute hydrochloric acid. Microscopic buff-colored prisms were obtained which did not melt below 320° C.

In the preparation of an emulsion containing the stabilizers used according to our invention, a solution of the stabilizer in a suitable solvent, such as alcohol or an alcohol-water mixture, adjusted to a neutral or slightly alkaline pH, i. e., pH 7.5 to 10, is made up and the solution mixed with the emulsion at any point during its preparation, but preferably during ripening or just prior to coating in concentrations varying from 25 mg. to 250 mg. per liter of emulsion. The actual concentration employed will depend upon the type of emulsion used and varies somewhat with the compound used.

The method of testing the stabilizers employed in the following examples consists of coating two film strips, such as cellulose acetate, with the same emulsion, one with and one without any stabilizer, storing the emulsions in an incubator for six days at 50° C., then exposing, developing, fixing, and washing the same under standard conditions. The fog density or blackening produced in the unexposed areas in the two emulsions is then measured in a transmission densitometer of standard type.

The following examples will serve to illustrate certain ways in which the stabilizers of our invention have been applied, but are not to be construed as limiting the invention.

Example IV

To 1 kilogram of an ordinary gelatin silver-bromoiodide emulsion, 100 mgs. of the compound of Example I were added just prior to coating. This emulsion, coated on a suitable support, was incubated for 3 to 5 days at 50° C. At the same time, a similar coating with the same emulsion but containing no stabilizer was also incubated as a reference type. Both emulsions immediately after coating gave a fog density of 0.02 upon photographic development. After the incubation period, these two coatings were exposed and developed together in a suitable developer. It was noted that the reference type containing no stabilizer had a fog density of 0.28, whereas the stabilized coating had a fog density of only 0.08.

Example V

Example IV was repeated with the exception that an equivalent quantity of the compound of Example III was substituted for the compound of Example I. After incubation, exposing and developing side by side with a reference emulsion containing no stabilizer, the emulsion containing the stabilizer had a fog density of only 0.04 whereas the unstabilized type had a fog density of 0.30.

Example VI

Example IV was repeated with the exception that an equivalent quantity of the compound of Example II was substituted for the compound of Example I. The results obtained were almost identical with those obtained in Example I.

Further experiments have shown that emulsions containing stabilizers in accordance with our invention have not only improved keeping qualities (i. e., a reduction in the fog produced by incubation or by long storage) but have greatly diminished and, in some cases, completely eliminated changes of speed to which some emulsions are susceptible.

The stabilizers, which we have described and

employed may be used in various kinds of emulsions. In addition to being useful in orthochromatic and panchromatic emulsions, they may also be used in non-sensitized emulsions and X-ray emulsions. If used with sensitizing dyes they may be added to the emulsion before or after the dyes are added. The dispersing agents for the silver-halides may be gelatin or other colloid such as water-soluble cellulose derivatives, e. g., hydroxy ethyl cellulose, methyl cellulose, carboxy-oxy-cellulose, low acetyl value cellulose acetate, and the like. The stabilizers may also be employed in gelatin or other colloid, such as polyamides or a mixture of gelatin with a polyamide as described in United States Patent 2,289,775; polyvinyl alcohol and jelling compound as described in United States Patent 2,249,537; polyvinyl acetaldehyde acetal resins and partially hydrolyzed acetate resins described in United States Patents 1,939,422 and 2,036,092; cellulose derivatives e. g., cellulose nitrate, cellulose acetate, the lower fatty acid esters of cellulose including simple and mixed esters, ethers of cellulose, and the like, as an under or overcoat for the emulsion, or as backing layer for the support. Moreover, they may be incorporated in the support for the sensitive emulsion layer or in an intermediate layer between the sensitive emulsion layer and the support, such as baryta coating commonly used in photographic papers, or they may be incorporated in a protective layer coated upon the emulsion surface, or the otherwise finished photographic material may be bathed in an alcohol or alcohol-water solution containing the stabilizer.

In the accompanying drawing, the various figures are enlarged section views of photographic materials having antifogging layers made according to our invention.

As shown in Figure 1, the support 1, which may be of any suitable material such as glass, cellulose ester, synthetic resin, or paper, is provided with an anti-fogging layer 3, containing one of said 5,7-diketo-3,4,6-triaza-indolizines referred to above. The light-sensitive emulsion layer 2 is attached to the anti-fogging layer 3.

Figure 2 illustrates a similar material in which the support 1 is coated with a light-sensitive emulsion layer 2, and on the latter side there is provided an anti-fogging layer 3, containing one of said 5,7-diketo-3,4,6-triaza-indolizines.

Figure 3 illustrates a film or plate of which the support 1 bears on one side the light-sensitive emulsion layer 2, and on the other side an anti-fogging layer 3 containing such 5,7-diketo-3,4,6-triaza-indolizine.

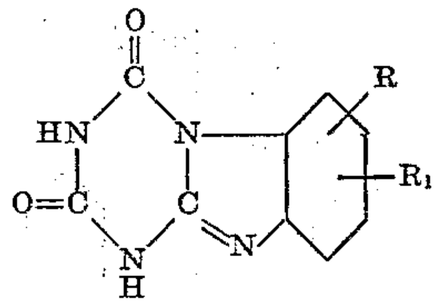
Figure 4 illustrates a film, plate or paper of which the support 1 is provided with the light-sensitive emulsion layer 2 containing as an anti-fogging layer such 5,7-diketo-3,4,6-triaza-indolizines.

Since the presence of these new compounds tends to prevent chemical fog whether they are incorporated directly into the emulsion, added to a separate surface or substratum layer, it is understood that the term "photographic material" as employed herein and in the appended claims, is used in a generic sense to include each of these possible applications.

Various modifications of this invention will occur to persons skilled in the art and it is, therefore, understood that the patent granted shall only be limited by the appended claims.

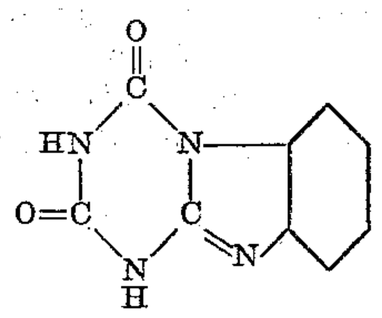
We claim:

1. A photographic material comprising a base and a light-sensitive silver-halide emulsion carried thereby, said photographic material containing, in fog inhibiting amount, a compound of the formula:

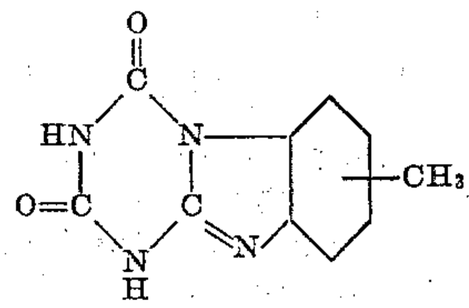


wherein R is a member selected from the class consisting of hydrogen and halogen, and R_1 is a member selected from the class consisting of hydrogen, aliphatic, alkoxy, carbalkoxy, carboxy and halogen groups.

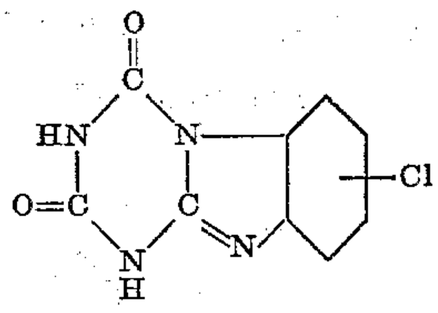
2. A photographic material comprising a base and a light-sensitive silver-halide emulsion carried thereby, said photographic material containing, in fog inhibiting amount, a 5,7-diketo-3,4,6-triaza-indolizine of the formula:



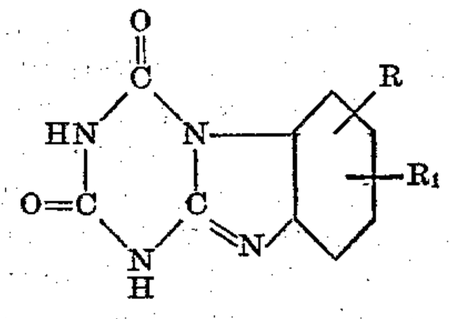
3. A photographic material comprising a base and a light-sensitive silver-halide emulsion carried thereby, said photographic material containing, in fog inhibiting amount, a 5,7-diketo-3,4,6-triaza-indolizine of the formula:



4. A photographic material comprising a base and a light-sensitive silver-halide emulsion carried thereby, said photographic material containing, in fog inhibiting amount, a 5,7-diketo-3,4,6-triaza-indolizine of the formula:

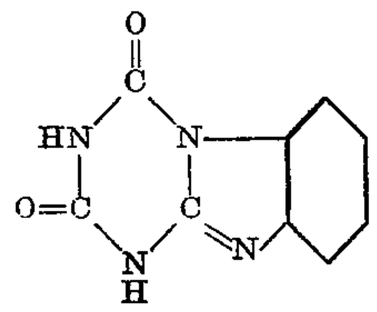


5. A photographic material comprising a base and a light-sensitive silver-halide emulsion containing, in fog inhibiting amount, a 5,7-diketo-3,4,6-triaza-indolizine having the general formula:

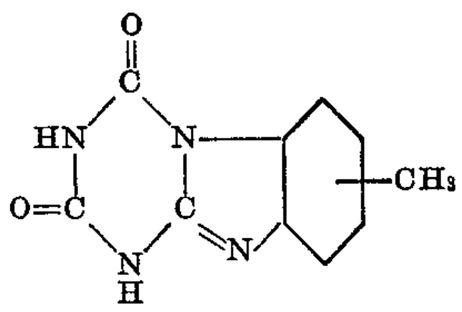


wherein R is a member selected from the class consisting of hydrogen and halogen, and R_1 is a member selected from the class consisting of hydrogen, aliphatic, alkoxy, carbalkoxy, carboxy and halogen groups.

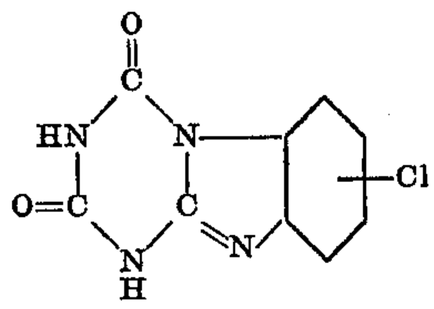
6. A photographic material comprising a base and a light-sensitive silver-halide emulsion containing, in fog inhibiting amount, a 5,7-diketo-3,4,6-triaza-indolizine of the formula:



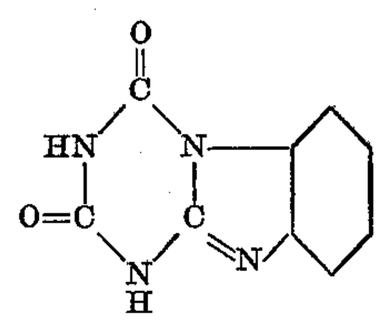
7. A photographic material comprising a base and a light-sensitive silver-halide emulsion containing, in fog inhibiting amount, a 5,7-diketo-3,4,6-triaza-indolizine of the formula:



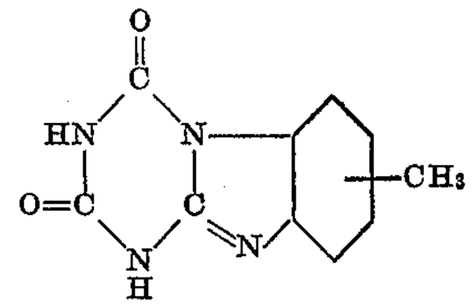
8. A photographic material comprising a base and a light-sensitive silver-halide emulsion containing, in fog inhibiting amount, a 5,7-diketo-3,4,6-triaza-indolizine of the formula:



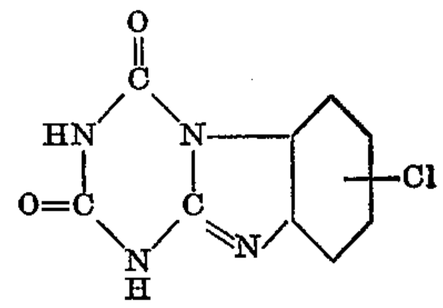
9. A photographic gelatino silver-halide emulsion containing from about 25 mgs. to about 250 mgs. per liter of emulsion of a 5,7-diketo-3,4,6-triaza-indolizine of the formula:



10. A photographic gelatino silver-halide emulsion containing from about 25 mgs. to about 250 mgs. per liter of emulsion of a 5,7-diketo-3,4,6-triaza-indolizine of the formula:



11. A photographic gelatino silver-halide emulsion containing from about 25 mgs. to about 250 mgs. per liter of emulsion of a 5,7-diketo-3,4,6-triaza-indolizine of the formula:



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The following references are of record in the file of this patent:

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Number	Name	Date
2,390,707	Heimbach	Dec. 11, 1945