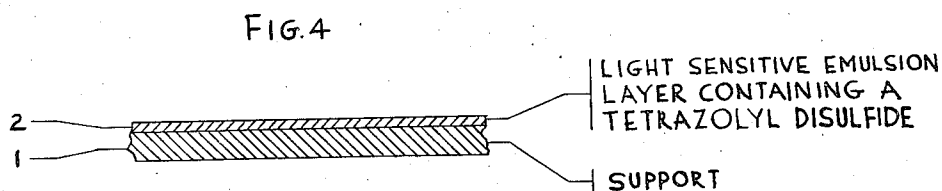
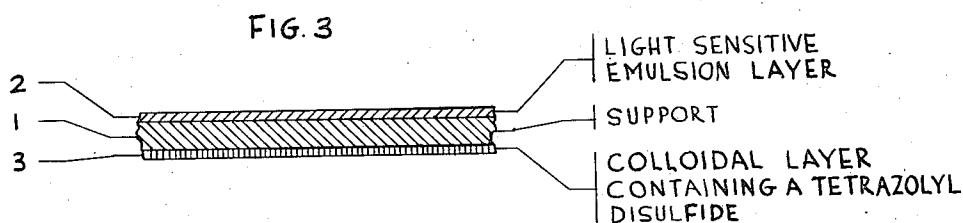
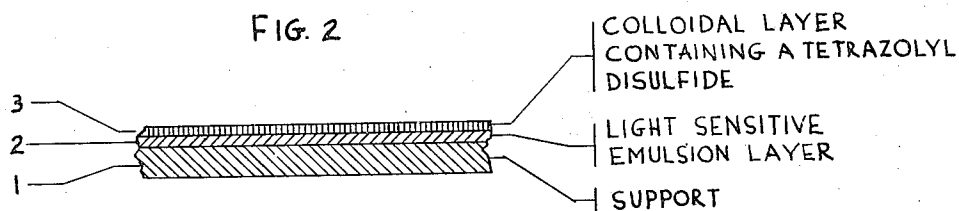
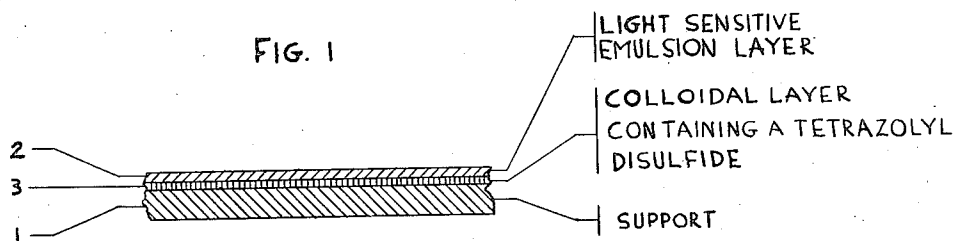


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TETRAZOLYL DISULFIDES AS STABILIZING AGENTS
FOR SILVER-HALIDE EMULSIONS
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2,465,149

TETRAZOLYL DISULFIDES AS STABILIZING AGENTS FOR SILVER-HALIDE EMULSIONS

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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 tetrazolyl disulfides as stabilizers for silver-halide emulsions.

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 emulsions, or by the storage of the film, particularly at high temperatures or for unusually long periods of time.

It is also known that mercapto tetrazoles and tetrazoles containing at least one =NH group, the hydrogen atom of which is capable of substitution by silver, have been described as being effective in preventing an increase in fog and thus stabilizing or controlling the keeping quality of light-sensitive silver-halide emulsions. Although these compounds have the ability to give the emulsions to which they are added stability and a steeper gradation, they have a definite shortcoming in that they, to some extent, lower the sensitivity of the emulsions.

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.

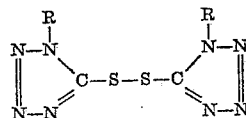
A further object is to provide stabilizers or anti-fogging agents for light-sensitive silver-halide emulsions, which do not lower the sensitivity of the emulsion, and which increase its stability.

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

We have found that the above objects are ac-

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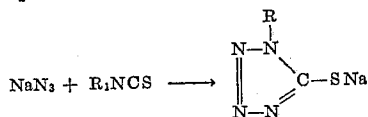
complished by the use of a combination of both the tetrazole and disulfide residues in the form of tetrazolyl disulfides which are superior in fog reducing tendency to either residue when used in conjunction with some other group. The bis [1-substituted-tetrazolyl-5] -disulfides utilized in accordance with the present invention have the following structural formula:



where R is a hydrocarbon radical, e. g., methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec.-butyl, tert.-butyl, amyl, hexyl, heptyl, octyl, nonyl, allyl, propargyl, butenyl, pentenyl, hexenyl, phenyl, o-, m-, and p-tolyl, naphthyl, α -naphthyl, β -naphthyl, diphenyl, benzyl, methylbenzyl, ethylbenzyl, and the like.

There are two general methods by which the tetrazolyl disulfides may be prepared. The first method applies to those tetrazolyls where R in the above general formula is aliphatic, and the second method to those where R is aromatic.

The first method is described by R. Stollé in the J. prakt. Chem., 133, p. 60, 1932, and consists of adding dropwise a solution of any aliphatic isothiocyanate in 95% alcohol to a hot, well-stirred, alcoholic suspension of sodium azide and heating the mixture under reflux for a period of time ranging from 2 to 8 hours. The reaction involved proceeds as follows:

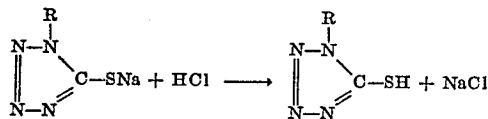


wherein R and R₁ are of the same value as R above.

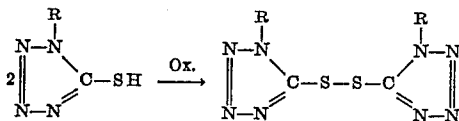
During the reflux period, a strong stream of CO₂ is passed through the well-stirred reaction mixture. At the end of the reflux period, the mixture is filtered hot and the hot filtrate evaporated to dryness. The residue is taken up in water (filtered, if necessary) and extracted several times with ether. The water solution is freed of ether and then acidified with HCl. The acidified solution is evaporated to dryness and

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the solid or sticky residue is purified by crystallization from ether or chloroform to yield the mercaptan.



Oxidation of the mercaptan to the tetrazolyl disulfide proceeds thus:



and may be effected by treatment of the water solution of the mercaptan with ferric chloride solution or with hydrogen peroxide. The disulfide precipitates from solution and may be crystallized from alcohol.

The second method is described by the same author on page 61 of the same publication and is similar to the first method with the exception that any aromatic isothiocyanate is substituted for an aliphatic isothiocyanate, the passage of CO₂ is omitted, and the reflux time reduced to 2 hours. On acidification, a solid product precipitates. This is recrystallized directly to yield the mercaptan in pure form.

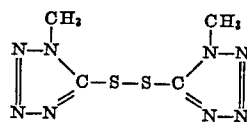
Oxidation of this mercaptan to the disulfide may be effected by treatment with hydrogen peroxide or dilute nitric acid. The resulting disulfide is best recrystallized from ethyl alcohol.

In the preparation of the tetrazolyl disulfides, utilized in accordance with the present invention, any aliphatic or aromatic isothiocyanate may be employed as the starting material. The nature of the isothiocyanate is immaterial, so long as the hydrocarbon radical is of the alkane, cycloalkane, alkene, alkenyl or aryl type.

As examples of suitable isothiocyanates may be mentioned isothiocyanic acid methyl ester, ethyl ester, propyl ester, isopropyl ester, butyl ester, isobutyl ester, sec.-butyl ester, tert.-butyl ester, amyl ester, isoamyl ester, hexyl ester, heptyl ester, octyl ester, nonyl ester, decyl ester, allyl ester, propargyl ester, phenyl ester, benzyl ester, xenyl ester, o-tolyl ester, p-tolyl ester and the like.

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



Bis-[1-methyl-tetrazolyl-5]-disulfide

An alcoholic solution of 15 grams of isothiocyanic methyl ester was added dropwise to a suspension of 19.5 grams of sodium azide in 250 cc. of 95% ethyl alcohol contained in a 3-necked 1 liter round-bottom flask fitted with an efficient stirrer, reflux condenser and inlet tube for the admission of CO₂. The mixture was stirred well throughout this operation and the subsequent 8 hour reflux period. Carbon dioxide was then passed through the mixture in a strong stream and the temperature of the mixture raised to the reflux point. Reflux was continued for 8 hours.

At the end of this time, the suspension was

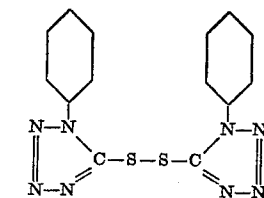
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filtered while still hot and the alcoholic filtrate evaporated to dryness on a water bath under reduced pressure. The residue was taken up in water and extracted twice with 50 cc. portions of ether to remove unreacted methyl isothiocyanate.

The ether was removed from the aqueous solution by passing through it a stream of air. The aqueous solution was made acid (Congo red paper) with HCl, and the resulting solution evaporated to dryness on a water bath under reduced pressure. Extraction of the resulting mass with boiling chloroform, followed by chilling of the extract, resulted in the formation of white crystals of 1-methyl-5-mercaptotetrazole.

A solution of 2 grams of methyl-1-mercapto-5-tetrazole in 30 cc. of water was warmed for 10 minutes with a mixture of 2 cc. of 30% hydrogen peroxide with 5 cc. of water. On cooling the mixture in ice, a precipitate appeared which was filtered and crystallized from ethyl alcohol.

Example II

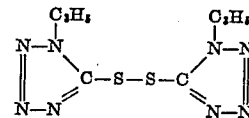


Bis-[1-phenyl-tetrazolyl-5]-disulfide

A solution of 13.5 grams of isothiocyanic phenyl ester in 150 cc. of 95% ethyl alcohol was added dropwise to a well-stirred suspension of 10 grams of sodium azide in 50 cc. of absolute alcohol contained in a 3-necked 500 cc. round-bottom flask equipped with an efficient stirrer and reflux condenser. The temperature of the well-stirred mixture was then raised to the reflux point and maintained there for two hours. At the end of this time, the mixture was filtered hot and the filtrate evaporated to dryness on the water bath under reduced pressure. The solid residue was taken up in water and the unreacted phenyl isothiocyanate removed by extraction with two 50 cc. portions of ether. The aqueous layer was acidified with HCl and the precipitate formed was collected on a Buchner funnel, washed with a little water and finally recrystallized from dilute ethyl alcohol.

Ten grams of the mercaptan was suspended in 500 cc. of a 10% nitric acid solution and, with good agitation, the temperature of the mixture raised to the boiling point. Immediately the suspension was filtered, the yellow solid remaining on the Buchner funnel was washed free of acid with water and crystallized from 95% ethyl alcohol.

Example III



Bis-[1-allyl-tetrazolyl-5]-disulfide

Example I was repeated with the exception that 20 grams of isothiocyanic acid allyl ester was substituted for 15 grams of isothiocyanic methyl ester.

The tetrazolyl disulfides which are substituted in the 1-position by an aliphatic hydrocarbon radical are dissolved in alcohol, such as methyl, ethyl, propyl, butyl and the like or in a water

mixture thereof, and the solutions thus obtained mixed with the emulsion at any point during its preparation.

Where, however, the 1-position of the tetrazolyl disulfide is substituted by an aryl radical, such compound is best dissolved in acetone. In the preparation of an emulsion containing the stabilizers, a solution of the stabilizer may be mixed with the emulsion at any point during its preparation, but preferably during ripening or just prior to coating in concentrations varying from $\frac{1}{2}$ to 500 mgs. per liter of emulsion. The actual concentrations employed will depend upon the type of emulsion, and may vary slightly with the compound used.

Beneficial effects in gray fog reduction may be obtained when solutions of these tetrazolyl disulfides are incorporated in the silver-halide emulsions as "ripening finals" or as "coating finals." By "ripening final" is meant an addition made during the "ripening" or "sensitivity-increasing" stage of the emulsion making process. Such additions may be designed to increase the sensitivity of the emulsion or to minimize gray fog formation. By "coating final" is meant an addition made to the emulsion just prior to coating it on a suitable support (glass, film, etc.) when the emulsion has nearly obtained its maximum sensitivity. The functions of these coating finals are nearly the same as those of the ripening finals, i. e., to increase sensitivity or to minimize fog formation.

When used as ripening finals, the tetrazolyl disulfides are best used in a concentration of $\frac{1}{2}$ -5 mg. per kilogram of wet emulsion, and when used as coating finals in a concentration of 10-100 mg. per kilo of wet emulsion.

Special advantage seems to be gained when plates coated with emulsion containing tetrazolyl disulfides are processed after standing for long periods of time. There is a marked reduction in gray fog as compared with a processed plate coated with emulsion with no added tetrazolyl disulfide. These advantages seem to be gained with a very minimum loss of sensitivity and contrast.

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 or our invention have been applied.

Example IV

A photographic film coated with an ordinary gelatin-bromiodide emulsion of normal speed and contrast on development under standard conditions, after incubation for six days at 50° C., gave a fog of 0.28 density. Another film coated with the same emulsion containing an addition of 100 mg. of bis-[1-methyl-tetrazolyl-5] disulfide per 1000 cc. of emulsion equivalent to about 50 grams of silver nitrate and developed under the same conditions, after the same incubation, gave a fog of only 0.08 density.

Example V

Example IV was repeated with the exception that an equivalent quantity of bis-[1-phenyl-tetrazolyl-5]-disulfide was substituted for bis-[1-methyl-tetrazolyl-5]-disulfide. The results obtained were almost identical with those obtained in Example IV.

Example VI

Example IV was again repeated with the exception that 75 mg. of bis-[1-allyl-tetrazolyl-5]-disulfide was substituted for 100 mg. of bis-[1-methyl-tetrazolyl-5]-disulfide. After incubation and development, the emulsion containing bis-[1-allyl-tetrazolyl-5]-disulfide gave a fog of only 0.08 density.

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-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, and the lower fatty acid esters of cellulose including simple and mixed esters and 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 the 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 the tetrazolyl disulfides 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

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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 tetrazolyl disulfides.

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 tetrazolyl disulfides.

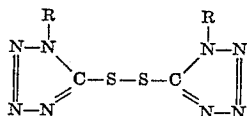
Figure 4 illustrates a film, plate or paper of which the support 1 is provided with the light-sensitive emulsion layer 2 containing as an anti-fogging layer such tetrazolyl disulfides.

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.

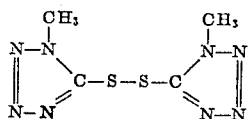
We claim:

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 tetrazolyl disulfide having the general formula:

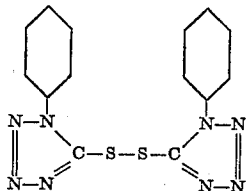


where R represents a hydrocarbon radical.

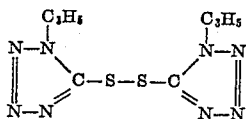
2. A photographic material comprising a base and a light-sensitive silver-halide emulsion carried thereby, said photographic material containing, in fog inhibiting amount, a tetrazolyl disulfide having the formula:



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 tetrazolyl disulfide having the formula:



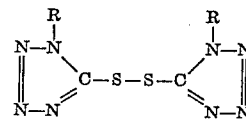
4. A photographic material comprising a base and a light-sensitive silver-halide emulsion carried thereby, said photographic material containing, in fog inhibiting amount, a tetrazolyl disulfide having the formula:



5. A photographic material comprising a base and a light-sensitive silver-halide emulsion con-

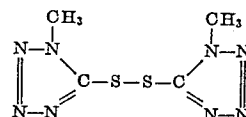
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taining, in fog inhibiting amount, a tetrazolyl disulfide having the general formula:

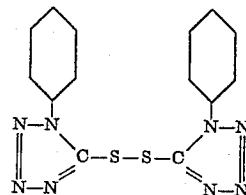


where R represents a hydrocarbon radical.

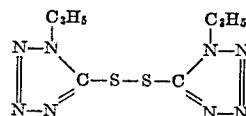
6. A photographic material comprising a base and a light-sensitive silver-halide emulsion containing, in fog inhibiting amount, a tetrazolyl disulfide of the formula:



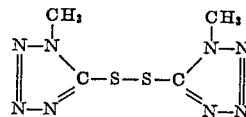
7. A photographic material comprising a base and a light-sensitive silver-halide emulsion containing, in fog inhibiting amount, a tetrazolyl disulfide of the formula:



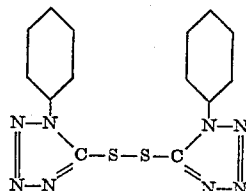
8. A photographic material comprising a base and a light-sensitive silver-halide emulsion containing, in fog inhibiting amount, a tetrazolyl disulfide of the formula:



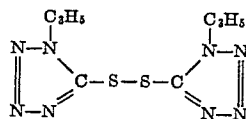
9. A photographic gelatino silver-halide emulsion containing from about 1/2 mg. to about 500 mgs. per liter of emulsion of a tetrazolyl disulfide of the formula:



10. A photographic gelatino silver-halide emulsion containing from about 1/2 mg. to about 500 mgs. per liter of emulsion of a tetrazolyl disulfide of the formula:



11. A photographic gelatino silver-halide emulsion containing from about 1/2 mg. to about 500 mgs. per liter of emulsion of a tetrazolyl disulfide of the formula:



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