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DEHYDRODITHIZONE AND MERCAPTOTETRAZOLIUM SALTS AS SILVER HALIDE PHOTOGRAPHIC ANTIFOGGANTS AND STABILIZERS

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ABSTRACT OF THE DISCLOSURE

Stabilizer and antifogging compounds for use in silver halide photography include dehydrodithizone and chloride, bromide and iodide salts for 5-alkyl mercapto-2,3-diaryltetrazole, 5-alkyl-mercapto-2,3 - dialkyltetrazole, 5-carboxyalkylmercapto-2,3-diaryltetrazole and 5-carboxyalkylmercapto-2,3-dialkyltetrazole compounds.

This invention relates in general to photography and in particular to the provision of novel stabilizing compounds for use in connection with the preparation and/or processing of photographic silver halide emulsions.

It is well known that light-sensitive materials such as gelatin-silver halide emulsions exhibit a marked tendency to fog. The term "fog" as used in the photographic art connotes that portion of the density obtained upon development which arises by virtue of factors other than the photographic exposure. The fog may be attributable to a number of influences including for example, excessive ripening of the emulsion, prolonged storage of the film and especially under conditions of elevated temperature and/or humidity, as well as by prolonged development of the exposed emulsion and the like. In general, the fog may be of two types, namely, yellow fog and chemical (gray) fog. The yellow fog, sometimes referred to as colored 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 the 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.

On the other hand, the so-called chemical fog, or gray fog, is the more common and is formed in a number of ways. As mentioned hereinbefore, such fog may be caused by the nucleation of silver on or in the silver halide grains due to inadvertent exposure, excessive ripening of the emulsion, storage of the film under severe conditions of temperature and/or humidity, etc. Fog may also be caused by exposure to chemicals, for example, hydrogen sulfide and other reactive sulphur compounds, hydrogen peroxide vapors and strongly reducing materials such as those present in the developer solution. In any event, and irrespective of the cause, the fog will usually manifest itself as a spurious density extant over the entire area of the sensitive coating and typically, is substantially nonuniform.

To overcome or otherwise alleviate the aforedescribed disadvantages it has become a recognized practice in the photographic art to add certain chemical stabilizer compounds to the light-sensitive emulsion at some stage of its preparation which purportedly function to enhance their photographic stability to an appreciable extent. However, in the vast majority of instances, the stabilizing and antifogging compounds heretofore employed for such purposes have provided only marginal improvement since

they are often characterized by the disadvantage that upon addition to the emulsion they cause a loss of speed and/or contrast of the emulsion or otherwise deleteriously affect its sensitometric characteristics. The loss in speed is particularly pronounced in those regions of the spectrum to which the emulsions are optically or dye sensitized.

In accordance with the discovery forming the basis of the present invention, it has been found that the antifogging and stabilization characteristics of light-sensitive silver halide emulsions can be synergistically modified to advantage by the utilization of a particular class of chemical compounds in connection with the preparation and/or processing of such emulsions.

Thus, a primary object of the present invention resides in the provision of improved antifogging and stabilizer compounds in which the foregoing and related disadvantages are eliminated or at least mitigated to a substantial degree.

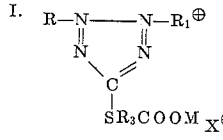
Another object of the present invention resides in the provision of light-sensitive silver halide emulsions containing a compound which stabilizes the emulsion against fogging while exhibiting little, if any, tendency to reduce the speed or contrast of such emulsions.

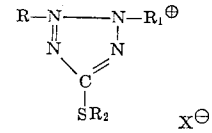
A further object of the present invention resides in the provision of light-sensitive silver halide emulsions and photographic elements prepared therewith containing an antifogging compound which is substantially devoid of any tendency to reduce the sensitivity of the emulsion to light of longer wave length due to the presence of one or more sensiizing dyes.

A still further object of the present invention resides in the provision of a process for the treatment of an exposed photographic silver halide emulsion wherein at least one of the steps of pretreating or developing the emulsion is effected in the presence of a novel stabilizing compound to be more fully described hereinafter.

The attainment of the foregoing and related objects is made in accordance with the broader aspects of the present invention by the incorporation in a light-sensitive photographic element, e.g., silver halide emulsion, developing solution and/or pretreatment solution of a compound selected from the group consisting of (a) 5-alkylmercapto-2,3-diaryltetrazolium salts, (b) 5-alkylmercapto-2,3-dialkyltetrazolium salts, (c) 5-carboxyalkylmercapto-2,3-diaryltetrazolium salts, (d) 5-carboxyalkylmercapto-2,3-dialkyltetrazolium salts and (e) dehydrodithizone.

The compounds encompassed by (a), (b), (c), and (d) can, for convenience, be represented according to the following structural formulae:

I. 

II. 

wherein R, R_1 and R_2 represent alkyl, e.g., methyl, ethyl, propyl, isopropyl, butyl, isobutyl, amyl, hexyl, undecyl, dodecyl, etc., and preferably lower alkyl of 1 to 4 carbon atoms; aryl, e.g., phenyl, naphthyl which may further contain inert substituents such as amino, hydroxy, alkoxy, acyl, acylamino and the like; R_3 represents lower alkylene, branch or straight chained, substituted or unsubstituted, e.g., methylene, ethylene, isobutylene, etc.; X represents an anion such as a halide atom, e.g., chloride, bromide or iodide, and M represents hydrogen or a water-solubilizing cation such as alkali metal, e.g., sodium, potassium, etc.; ammonium, substituted ammonium, etc.

The compounds encompassed by each of the above formulae can be prepared according to techniques which

are well known in the art. In this connection, reference is made to the syntheses described in Journal of the American Chemical Society, vol. 83, pp. 5023 to 5026; and "Dissertation," John Reinheimer, The Johns Hopkins University, 1948.

The compound dehydrodithizone as reported in the literature is capable of several formulistic definitions. In this connection specific reference is made to J.A.C.S., vol. 83, p. 5023. Despite the fact that several theories are postulated in explanation of the validity of a given structural representation, it is nevertheless manifest that the term dehydrodithizone connotes a specific species of tetrazolium salts.

Improved fog reduction and other beneficial effects are obtained when the aforementioned compounds are incorporated into the silver halide emulsion as "ripening finals" or as "coating finals." As is well known, ripening finals are added during the ripening or sensitivity increasing stage of the emulsion making process. Such additions may be effected before, during or after the decomposition of the soluble silver salt such as silver nitrate by means of a soluble halide such as potassium bromide, sodium chloride or the like in the presence of a suitable colloid carrier such as gelatin, polyvinyl alcohol, solubilized casein albumen or the like.

Coating finals are added to the emulsion just prior to coating on a suitable support such as glass, paper or film at a time when the emulsion has nearly attained its maximum sensitivity.

It will also be understood that the novel stabilizers of the present invention may be incorporated in a layer adjacent to the sensitized layer such as an anti-abrasion layer. The stabilizing compound may be utilized in concentrations varying over a relatively wide range; for example, when added to the light-sensitive silver halide emulsion layer as a ripening final, it is found that optimum realization of results provided herein are assured with stabilizer concentrations ranging from as low as .02 milligram up to about 500 milligrams per 0.6 mole of silver halide. The concentration selected within the aforestated range will depend to a large extent on the type of emulsion employed and thus it is advisable to determine the optimum concentration from case to case. If added during the emulsion preparation stage, stabilizer concentrations on the order of approximately one-tenth of those employed when adding the stabilizer as a coating final are found to be quite suitable.

The stabilizer compounds contemplated herein can be applied in a variety of ways to impart stability to photographic elements. As previously mentioned, they may be included as a constituent of the emulsion layer, of a surface layer over the emulsion or alternatively, over the base or support.

Further embodiments of the present invention contemplate the addition of such compounds to at least one of the developing, fixing, washing, drying, etc. solutions utilized in the processing of the exposed emulsion. For example, when utilized in the washing step the stabilizer can be applied to the otherwise finished photographic element by immersing same in an alcohol, e.g., methanol or alcohol-water solution in the case of the free acid derivatives while the salt derivatives may be employed effectively as simple water solutions.

In general, it is found that the improvements provided by the present invention are particularly manifest according to procedures whereby development is effected in the presence of said stabilizer compounds. This, of course, would be the case should the stabilizer be included in the light-sensitive photographic element, the developing solution and/or suitable developer pre-bath. In any event, when incorporated into the photographic developer or other processing bath, the stabilizers of the present invention are preferably employed in concentrations ranging from about 1 to about 50 milligrams per liter of solution, with a range of about 5 milligrams to about 20 milligrams per liter being particularly preferred.

In addition to being useful in orthochromatic and panchromatic emulsions, the stabilizers may also be used in non-sensitized emulsions, X-ray emulsions, paper emulsions, color emulsions and the like. If used with sensitizing dyes, they may be added to the emulsion before or after dye addition. Moreover, the present stabilizers may also be employed in conjunction with other known antifoggants and stabilizers, reduction stabilizers, metal and noble metal sensitizers or in combination with other additive agents and the like.

The stabilizer may also be employed in gelatin or other water-permeable colloids including polyamides or a mixture of gelatin with a polyamide as described in U.S. Patent 2,289,775; polyvinyl alcohol and gelling compound as described in U.S. Patent 2,249,537; polyvinyl acetaldehyde acetal resins and partially hydrolyzed acetate resins described in U.S. 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 sample and mixed esters and ethers of cellulose and the like.

When preparing the photographic emulsion in accordance with the present invention, a solution of the stabilizer in a suitable solvent, such as water, alcohol, dimethyl formamide or alcohol-water mixture adjusted to a neutral or slightly alkaline pH, i.e. about 7.5 to 10, is made up and the solution mixed with the emulsion at any convenient stage during its preparation, but preferably during ripening or just prior to coating.

Although any of the aforedescribed compounds may be utilized to advantage in the practice of the present invention, particularly beneficial results are obtained and especially with regard to the suppression of fog which would otherwise result from film storage under severe conditions of humidity and temperature with the 1,3-diphenyl . . . derivatives. As particular examples of such compounds there may be mentioned without limitation the following:

5-methylmercapto-3,3-diphenyltetrazolium iodide
5-ethylmercapto-2,3-diphenyltetrazolium iodide
5-carboxymethylmercapto-2,3-diphenyltetrazolium iodide
5-carboxyethylmercapto-2,3-diphenyltetrazolium iodide

The following examples are given for purposes of illustration only and are not to be considered in any way as being limitative of the present invention.

EXAMPLE I

(A) Preparation of 5 - methylmercapto-2,3-diphenyltetrazolium iodide.—A solution was prepared consisting of dehydrodithizone (1.90 g.) and methyl iodide (1.26 g.) in 100 ml. dry chloroform. The solution thus prepared is refluxed in a 250 ml. flask on a steam bath for approximately 75 minutes. The solvents are then distilled off to give a dark red oil which yields 2.67 g. of solid upon addition of anhydrous ether. After crystallization with a mixture comprising 100 cc. isopropanol and 4 cc. of water, the solid obtained had a melting point of 219° C.

Analysis.—Calc. for $C_{14}H_{13}N_4SI$. Calc.: C, 42.4; H, 3.3; S, 8.1. Found: C, 42.05, 41.78; H, 3.45, 3.51; S, 7.90, 8.04.

(B) A silver halide emulsion in gelatin containing 2% silver iodide and 98% silver bromide is prepared in conventional manner and brought up to its maximum light sensitivity. It is then readied for coating; finals are added such as sensitizing dyes and hardening agents. Approximately 6 cc. of a 0.01% solution of 5-methylmercapto-2,3-diphenyltetrazolium iodide was added to the emulsion as an antifoggant and stabilizer. The emulsion samples contained about 0.6 mole of silver halide. The so prepared emulsion samples were then coated on a suitable

cellulose ester base and dried. Samples of these film coatings were then exposed in a Type IB sensitometer and developed in a developer of the following composition:

Metol	gram	1.5
Sodium sulfite, anhydrous	do	45
Sodium bisulfite	do	1
Hydroquinone	do	3
Sodium carbonate, monohydrated	do	6
Potassium bromide	do	0.8
Water to make 1 liter.		

Quantity of Compound Used	Fog at 12′ dev.	Oven fog at 3′ dev.	Relative speed at 3′ dev.
0	.28	.26	100
0.4 mg. per kilo	.26	.26	100
0.8 mg	.24	.25	93

EXAMPLE II

(A) Synthesis of Dehydrodithizone.—A solution was prepared consisting of:

$K_3Fe(CN)_6$	g	16
Na_2CO_3	g	15
water	ml	195
95% ethanol	ml	223

The solution thus prepared was added to a one-liter, 3 neck flask equipped with a stirrer, condenser, and gas inlet. The air in the flask was then evacuated and replaced with nitrogen whereupon 6.35 g. of diphenylthiocarbazone was added to the flask solution with stirring. Stirring is maintained at room temperature for approximately 48 hours whereupon there was obtained 5.3 g. of a dark solid which was filtered and washed with a cold water/ethanol solution. After two crystallizations with ethanol, the product obtained in the form of bright orange crystals, had a melting point of 180° C.

Analysis.—$C_{13}H_{10}N_4S$. Calc.: C, 61.6; H, 3.9. Found: C, 61.19, 61.03; H, 4.14, 3.88.

(B) Part B of Example I was repeated except that the 5-methylmercapto-2,3-diphenyltetrazolium iodide is replaced in the same amount with 0.001% solution of dehydrodithizone. After processing the following sensitometric results were obtained:

Quantity of Compound Used	Fog at 12′ dev.	Oven fog at 3′ dev.	Relative speed at 3′ dev.
0	.27	.24	100
0.02 mg. per kilo	.24	.21	100
0.08 mg	.22	.17	92

EXAMPLE III

A silver halide emulsion in gelatin containing 2% silver iodide and 98% silver bromide was coated onto a film base in a manner known to the art. After coating, a solution containing 20 grams of gelatin in 1 liter of H_2O to which had been added approximately 8 cc. of a 0.001% solution of dehydrodithizone was coated thereon as an anti-abrasion layer. After drying, the film samples were exposed and processed as described in Example I.

Quantity of Compound Used	Fog at 12′ dev.	Oven fog at 3′ dev.	Relative speed at 3′ dev.
0 mg	.20	.19	100
0.04 mg	.18	.18	94
0.1 mg	.12	.17	90

As the foregoing results make manifestly clear, significant reduction in the fog characteristic is obtained by the use of the novel antifogging agents of the present invention. Moreover, such improvement is realized in the absence of any deleterious effects upon emulsion speed.

Results similar to those described above are obtained when the stabilizer compounds of the present invention are added to one or more of the processing baths conventionally employed in the predevelopment and post-development of an exposed silver halide photographic film. As previously explained, significant stabilizing improvement is observed when such compounds are added either to the developer bath or prebath. Furthermore, results comparable to those described in the foregoing examples are obtained when the particular antifoggants described therein are substituted in equivalent amounts and within the range specified with one or more of the following compounds:

5-carboxyethylmercapto-2,3-diphenyltetrazolium chloride
5-ethylmercapto-2,3-diphenyltetrazolium iodide
5-propylmercapto-2,3-diphenyltetrazolium iodide
5-isobutylmercapto-2,3-diphenyltetrazolium iodide
5-carboxypropylmercapto-2,3-diphenyltetrazolium chloride . . . etc.

The developer composition may be any of those conventionally employed in the development of exposed silver halide emulsions and accordingly, may be of the hydroquinone type, i.e., those which contain hydroquinone, potassium metabisulfite and potassium bromide, or they may be of the metol-hydroquinone type, i.e., those which contain p-methylaminophenol, sodium sulfite, sodium bisulfite, hydroquinone sodium carbonate, and potassium bromide. Alternatively, the developer composition may be of the so-called borax type, i.e., those which contain p-methylaminophenol, sodium sulfite, hydroquinone borax and potassium bromide.

It will also be understood that the novel stabilizers of the present invention may be employed singly or in admixtures comprising two or more of such compounds. Again, optimum combinations thereof can be readily ascertained in a particular instance by routine laboratory experimentation.

The present invention has been disclosed with respect to certain preferred embodiments thereof, and there will become obvious to persons skilled in the art various modifications, equivalents, or variations thereof which are intended to be included within the spirit and scope thereof.

What is claimed is:

1. A process of treating an exposed silver halide emulsion which comprises developing said emulsion in the presence of an antifoggant and stabilizer comprising a compound selected from the group consisting of (a) dehydrodithizone, (b) 5-alkylmercapto-2,3-diaryltetrazolium chlorides, bromides and iodides, (c) 5-alkylmercapto-2,3-dialkyltetrazolium chlorides, bromides and iodides, (d) 5-carboxyalkylmercapto-2,3-diaryltetrazolium chlorides, bromides and iodides, (e) 5-carboxyalkylmercapto-2,3-dialkyltetrazolium chlorides, bromides and iodides and (f) the alkali metal, ammonium and substituted ammonium salts of the carboxy compounds of (d) and (e).

2. A process according to claim **1** wherein said antifoggant and stabilizer compound comprises 5-methylmercapto-2,3-diphenyltetrazolium iodide.

3. A process according to claim **1** wherein said antifoggant and stabilizer compound comprises dehydrodithizone.

4. An aqueous developer solution containing a silver halide photographic developing agent and an antifoggant and stabilizer comprising a compound selected from the group consisting of (a) dehydrodithizone, (b) 5-alkylmercapto-2,3-diaryltetrazolium chlorides, bromides and iodides, (c) 5-alkylmercapto-2,3-dialkyltetrazolium chlorides, bromides and iodides, (d) 5-carboxyalkylmercapto-2,3-diaryltetrazolium chlorides, bromides and iodides, (e) 5-carboxyalkylmercapto-2,3-dialkyltetrazolium chlorides, bromides and iodides and (f) the alkali metal, ammonium and substituted ammonium salts of the carboxy compounds of (d) and (e).

5. A light-sensitive silver halide emulsion containing an antifoggant and stabilizer comprising a compound selected from the group consisting of (a) dehydrodithizone, (b) 5-alkylmercapto-2,3-diaryltetrazolium chlorides, bromides

and iodides, (c) 5-alkylmercapto-2,3-dialkyltetrazolium chlorides, bromides and iodides, (d) 5-carboxyalkylmercapto - 2,3 - diaryltetrazolium chlorides, bromides and iodides, (e) 5-carboxyalkylmercapto-2,3-dialkyltetrazolium chlorides, bromides and iodides and (f) the alkali metal, ammonium and substituted ammonium salts of the carboxy compounds of (d) and (e).

6. A light-sensitive silver halide emulsion according to claim 5 wherein said antifoggant comprises 5-methylmercapto-2,3-diphenyltetrazolium iodide.

7. A light-sensitive silver halide emulsion according to claim 5 wherein said antifoggant comprises dehydrodithizone.

8. A light-sensitive photographic material comprising a base and a light-sensitive silver halide emulsion, said light-sensitive material containing an antifoggant and stabilizer comprising a compound selected from the group consisting of (a) dehydrodithizone, (b) 5-alkylmercapto-2,3-diaryltetrazolium chlorides, bromides and iodides, (c) 5-alkylmercapto-2,3-dialkyltetrazolium chlorides, bromides and iodides, (d) 5-carboxyalkylmercapto-2,3-diaryltetrazolium chlorides, bromides and iodides, (e) 5-carboxyalkylmercapto-2,3-dialkyltetrazolium chlorides, bromides and iodides and (f) the alkali metal, ammonium and substituted ammonium salts of the carboxy compounds of (d) and (e).

9. A light-sensitive photographic material according to claim 8 wherein said antifoggant and stabilizer compound is present in said light-sensitive silver halide emulsion layer.

10. A light-sensitive photographic material according to claim 8 wherein said antifoggant and stabilizer compound is present in a layer in contact with said light-sensitive silver halide emulsion layer.

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