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2,933,388

TETRAZAINDENE COMPOUNDS AND PHOTOGRAPHIC APPLICATION

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11 Claims. (Cl. 96—61)

This invention relates to tetrazaindene compounds, methods for making them, and to photographic silver halide emulsions and photographic treating baths containing them.

Silver halide emulsions are frequently subject to image degradation during processing, that is, during development, fixing, washing, toning, or other treatment and during the moist heat to which they are subjected on drying, such as when prints are subjected to ferrotyping or hot-type glazing. This degradation of the image frequently manifests itself as "plumming" or "bronzing" of the image.

It is also well known that photographic emulsions on storage tend to lose sensitivity and to become spontaneously developable without exposure to light. There is normally a detectable amount of the silver salt reduced during development in the areas where no exposure was given; this is commonly called "fog," and sometimes called "chemical fog" where it is necessary to distinguish between it and the effects of accidental exposure to radiation; in this invention, I am not concerned with the latter.

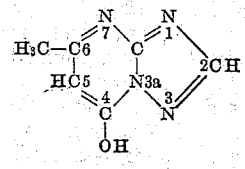
Fog depends both on the emulsion and the conditions of development; for a given emulsion it increases with the degree of development. With constant development conditions, it tends to increase with time, temperature and relative humidity of storage conditions; it is common practice to make accelerated tests of the stability of photographic emulsions by storage at increased temperature or humidity, or both. It is, of course, desirable to have emulsions as stable as possible under the conditions of high temperature and humidity which may occur in tropical climates, for example. Fog usually appears over the whole area of the sensitive coating, but when severe, it frequently is non-uniform. Fog may also be caused by exposure to chemicals, for example, hydrogen sulfide and other reactive sulfur compounds, hydrogen peroxide vapor, and strongly reducing materials. While antifoggants and stabilizers may protect, to some extent, against such effects, it is normally understood that an antifoggant protects against spontaneous growth of fog during prolonged storage or storage at high temperatures and humidities, or during development to maximum contrast and speed, or both.

It is, therefore, an object of my invention to provide certain new tetrazaindene compounds. A further object is to provide methods for making these new compounds. Still another object is to provide a means of avoiding the aforesaid "plumming" effect in photographic prints. Another object is to provide a method of stabilizing photographic silver halide emulsions during storage. Other objects will become apparent from a consideration of the following description and examples.

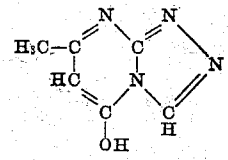
It is known that ethyl acetoacetate will condense with 3-amino-1:2:4-triazole to give a tetrazaindene derivative

to which the following two alternative formulas have been assigned:

(I)



(II)



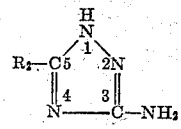
It is believed that the product most probably has the structure represented by Formula I, but it is possible that the OH group may be attached in the 6-position and the CH_3 group in the 4-position. I shall, therefore, designate the hydroxy-methyl-tetrazaindene obtainable by the condensation of ethyl acetoacetate with 3-amino-1:2:4-triazole as 4-hydroxy-6-methyl-1:3:3a:7-tetrazaindene (Formula I).

It has been found that, in general, acylacetic esters of the general formula:

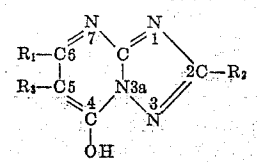
(III) $R_1COCHR_3COOC_2H_5$

wherein R_1 represents an alkyl (i.e., methyl, ethyl, n-propyl, n-butyl, etc., e.g., an alkyl group containing from 1 to 4 carbon atoms), aralkyl (i.e., benzyl, β-phenethyl, etc.) or aryl (i.e., phenyl, tolyl, chlorophenyl, etc., e.g., a mononuclear aromatic group of the benzene series) group, and R_3 represents a hydrogen atom, a halogen atom (e.g., chlorine, bromine, etc.) or an alkyl (i.e., methyl, ethyl, n-propyl, n-butyl, etc., e.g., an alkyl group containing from 1 to 4 carbon atoms) group, will condense with 3-amino-1:2:4-triazoles of the general formula:

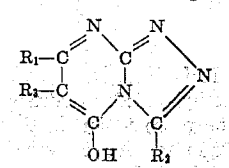
(IV)



wherein R_2 represents a hydrogen atom, an alkyl (i.e., methyl, ethyl, n-propyl, n-butyl, etc., e.g., an alkyl group containing from 1 to 4 carbon atoms), an aralkyl (i.e., benzyl, β-phenethyl, etc.), or aryl (i.e., phenyl, tolyl, chlorophenyl, etc., e.g., a mononuclear aromatic group of the benzene series), or an alkylthio (e.g., methylthio, ethylthio, etc.), aralkylthio (e.g., benzylthio, etc.), or arylthio (e.g., phenylthio, tolylthio, etc.) group, to give ring-substituted hydroxy-tetrazaindenes to which the following two alternative general formulae can be assigned:



(V)



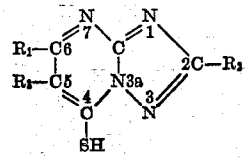
(VI)

wherein R_1, R_2 and R_3 have the values given above.

It is also believed that the products most probably have the structure represented by Formula V, but it is possible that the OH group may be attached in the 6-position and the group R_1 in the 4-position. I shall, therefore, designate the compounds obtainable by this condensation as

ring-substituted 4-hydroxy-1:3:3a:7-tetrazaindenes (the ring substituents being R_1, R_2 and R_3).

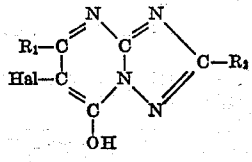
It is known that the hydroxyl group in 4-hydroxy-6-methyl-1:3:3a:7-tetrazaindene can be replaced by a chlorine atom and that this chlorine atom can, in turn, be replaced by an amino group or by a substituted amino group. It has now been found that the chlorine atom in this compound, and in compounds obtained by replacement with chlorine of the hydroxyl group in compounds of general Formula V, can be replaced by a mercapto group. It has also been found that the hydroxyl group can be directly replaced by a mercapto group. To the resulting ring-substituted mercapto-tetrazaindenes the following general formula has, in accordance with the considerations indicated above, been assigned.



(VII)

wherein R_1, R_2 and R_3 have the values given above.

The compounds of general Formula V wherein R_3 is a hydrogen atom can also be directly halogenated to give compounds of the general formula:

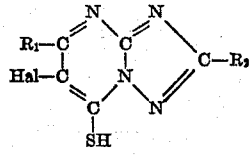


(VIII)

wherein R_1 and R_2 have the values given above, and Hal represents a halogen atom (e.g., bromine, chlorine, etc.), especially a bromine atom.

The hydroxyl group in the compounds of general Formula VIII can also be replaced by a mercapto group, either directly or by first replacing it by a chlorine atom and then, in turn, replacing this by a mercapto group, to give halogeno-ring-substituted mercapto-tetrazaindenes of the probable general formula:

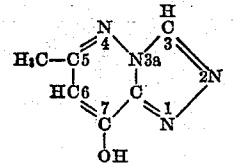
(IX)



wherein R_1 and R_2 have the values given above, and Hal represents a halogen atom (e.g., chlorine, bromine, etc.).

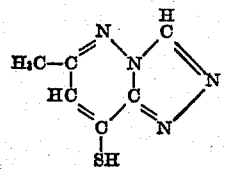
It is also known that ethyl acetoacetate will condense with 1-amino-1:3:4-triazole to give a tetrazaindene derivative of the formula:

(X)



It is likewise known that the hydroxyl group in 5-methyl-1:2:3a:4-tetrazaindene can be replaced by a chlorine atom which in turn can be replaced by a mercapto group to give 5-methyl-1:2:3a:4-tetrazaindene-7-thiol of the formula:

(XI)



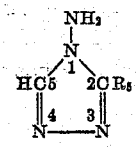
Bülow and Haas, who described the preparation of the compound as well as of the corresponding phenyl compound, in "Berichte der deutschen chemischen Gesellschaft," 1910, vol. 43, 1975, stated that it is easily oxidized. I have found that it is quite stable and has a melting point of 218° C.

It has now been further found that, in general, acylacetic esters of the general formula:

(XII) $R_1COCHR_4COOC_2H_5$

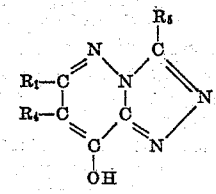
wherein R_1 has the values given above, and R_4 represents a hydrogen atom or an alkyl (i.e., methyl, ethyl, n-propyl, n-butyl, etc., e.g., an alkyl group containing from 1 to 4 carbon atoms) group, will condense with 1-amino-1:3:4-triazoles of the general formula:

(XIII)



wherein R_5 represents a hydrogen atom or an alkyl (i.e., methyl, ethyl, n-propyl, n-butyl, etc., e.g., an alkyl group containing from 1 to 4 carbon atoms), aralkyl (i.e., benzyl, β-phenethyl, etc.), or aryl (i.e., phenyl, tolyl, chlorophenyl, etc., e.g., a mononuclear aromatic group of the benzene series) group or an alkylthio (e.g., methylthio, ethylthio, etc.), aralkylthio (e.g., benzylthio, etc.) or arylthio (e.g., phenylthio, tolylthio, etc.) group, to give ring substituted hydroxy-tetrazaindenes of the general formula:

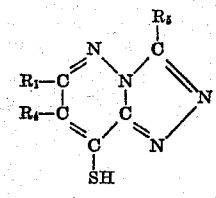
(XIV)



wherein R_1, R_4 and R_5 have the values given above.

It has further been found that the hydroxyl group in compounds of the general Formula XIV can be replaced by a chlorine atom and that this chlorine atom can, in turn, be replaced by a mercapto (thiol) group. It has also been found that the hydroxyl group can be directly replaced by a mercapto group. The resulting mercapto compound has the general formula:

(XV)



wherein R_1, R_4 and R_5 have the values given above.

It has further been found that a tetrazaindene compound comprising a diazine ring fused to a triazole ring so that said rings have a single nitrogen atom in common and having a thiol substituent attached to a carbon atom of said diazine ring, such as the compounds of the general Formulae VII and IX or of the general Formula XV or the salt of such a compound, for example, an alkali metal salt, can with advantage be incorporated in a photographic silver halide emulsion, or in a photographic treating bath.

It has now been found that by the incorporation in a photographic silver halide emulsion, especially a silver chloride or chloro-bromide emulsion of at least one tetrazaindene compound comprising a diazine ring fused to a triazole ring so that said rings have a single nitrogen atom in common and having a thiol substituent attached to a carbon atom of said diazine ring, such as the compounds of the probable general Formulae VII and IX or of the

general Formula XV or of their salts, such image degradation can be minimized or even prevented. The compounds are thus effective "anti-plumming" agents. They may be directly incorporated in an emulsion during its manufacture, or the emulsion may be bathed in their solutions in convenient solvents. The emulsion can be a gelatino-silver halide emulsion, but emulsions in which the carrier is polyvinyl alcohol, hydrolyzed cellulose acetate, or other hydrophilic colloid, can be used. When the compounds are incorporated in the emulsion, such as a gelatino-silver chloride emulsion containing small amounts of bromide or iodide, they can be used in amounts from 0.2 to 10 grams per unit of silver halide formed from 1000 grams of silver nitrate. When the emulsion is bathed in a solution of the compound, such as an aqueous alkaline solution, the solution can contain from about 0.01% up to about 1%, preferably about 0.1% by weight of the compound.

It has further been found that by the incorporation, in a photographic treating bath, such as a non-coupling developing bath (e.g., a hydroquinone developer) for photographic prints which are to be glazed, of at least one tetrazaindene compound comprising a diazine ring fused to a triazole ring so that said rings have a single nitrogen atom in common and having a thiol substituent attached to a carbon atom of said diazine ring, such as the compounds of the probable general Formulae VII and IX or of the general Formula XV or of their salts, the reflection density of the maximum black obtained in the developed print before glazing can be raised, and/or the contrast can be increased. Moreover, by the incorporation in a photographic non-coupling developing bath for photographic transparencies of at least one tetrazaindene compound comprising a diazine ring fused to a triazole ring so that said rings have a single nitrogen atom in common and having a thiol substituent attached to a carbon atom of said diazine ring, such as the compounds of the probable general Formulae VII and IX or of the general Formula XV or of their salts, the transmission density of the maximum black obtained on development can be raised, and/or the contrast can be increased, especially when the transparency is still wet. This is a very useful effect, for example, in X-ray plates.

According to one feature of the present invention, therefore, there is provided a ring-substituted mercapto-tetrazaindene of Formula VII or a water-soluble salt thereof, by replacement with the —SH group of the —OH group in the ring-substituted hydroxy-tetrazaindene, obtainable by the condensation of an acylacetic ester of the general formula $R_1COCHR_3COOC_2H_5$, wherein R_1 and R_3 have the values given above, with a 3-amino-1:2:4-triazole of Formula IV.

It will be noted that, owing to the labile character of the double bonds and the hydrogen atom in 1-position of the compounds of general Formula IV, the 3-position and 5-position are equivalent so that the compounds may also be designated 5-amino-1:2:4-triazoles.

According to a further feature of the invention there is provided a halogeno-ring-substituted mercapto-tetrazaindene of Formula IX, or a water-soluble salt thereof, by the replacement with the —SH group of the —OH group in the halogeno-ring-substituted hydroxy-tetrazaindene, obtainable by halogenation of the ring-substituted hydroxy-tetrazaindene (obtainable by the condensation of an acylacetic ester of the general formula

$$R_1COCH_2COOC_2H_5$$

wherein R_1 has the values given above, with a 3-amino-1:2:4-triazole of Formula IV).

The replacement of the OH group in compounds of the general Formula V can be effected by well-known methods which are described in the chemical literature. For example, it can be effected by the reaction of phosphorus pentasulphide on a compound of general Formula V. Alternatively, the hydroxyl group can first be replaced by a chlorine group, for example by the reaction of phosphorus oxychloride and/or phosphorus pentachloride on a compound of general Formula V, followed by replacement of the chlorine atom by a mercapto group, for example by the action of an alkali metal sulfide, such as potassium sulfide, or thiourea upon the resulting chloro compound.

According to a further feature of the invention, there is provided a compound of Formula XV or a water-soluble salt thereof.

Such compounds can be obtained by replacement with a mercapto group of the hydroxyl group in compounds of the general Formula XIV by the methods described above for replacement of the hydroxyl group in compounds of general Formula V.

The invention also includes the method of preparing the ring-substituted mercapto-tetrazaindenes of the probable general Formula VII which comprises heating with thiourea in a solvent the ring-substituted chloro-tetrazaindene obtainable by replacement with a chlorine atom of the —OH group in the ring-substituted hydroxy-tetrazaindene obtainable by the condensation of an acylacetic ester of the general formula $R_1COCHR_3COOC_2H_5$, wherein R_1 and R_3 have the values given above, with a 3-amino-1:2:4-triazole of Formula IV. The said ring-substituted hydroxytetrazaindene can be heated with phosphorus oxy-chloride, if desired together with phosphorus pentachloride, preferably in the presence of a tertiary organic base such as dimethylaniline, to replace the hydroxyl group with a chlorine atom, and the resulting ring-substituted chloro-tetrazaindene can be heated to reflux with thiourea and methanol to replace the chlorine atom with a mercapto group, the resulting ring-substituted mercapto tetrazaindene thereafter being isolated from the reaction mixture.

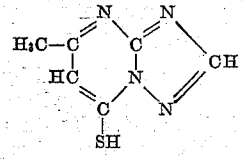
The invention also includes the method of preparing the halogeno-ring-substituted mercapto-tetrazaindenes of the probable general Formula IX which comprises heating with thiourea in a solvent, the halogeno-ring-substituted chloro-tetrazaindene obtainable by replacement with a chlorine atom of the —OH group in the halogeno-ring-substituted hydroxy-tetrazaindene obtainable by halogenation of the ring-substituted hydroxy-tetrazaindene obtainable by the condensation of an acylacetic ester of the general formula $R_1COCH_2COOC_2H_5$, wherein R_1 has the values given above with a 3-amino-1:2:4-triazole of Formula IV. Thus the ring-substituted hydroxy-tetrazaindene obtained by the condensation of an acylacetic ester of the general formula $R_1COCH_2COOC_2H_5$, wherein R_1 has the values given above, with a 3-amino-1:2:4-triazole of Formula IV can be brought into contact, in the form of a suspension or solution, with a halogen, the resulting halogenated compound being then heated with phosphorus oxychloride, preferably in presence of a tertiary organic base, whereafter the resulting halogeno-ring-substituted chloro-tetrazaindene is heated to reflux with thiourea and methanol and the resulting halogeno-ring-substituted mercapto-tetrazaindene is isolated from the reaction mixture. The said suspension or solution may be mixed with a solution of bromine. The solvent may be, for example, acetic acid.

The invention also includes a photographic silver halide emulsion containing at least one tetrazaindene compound comprising a diazine ring fused to a triazole ring so that said rings have a single nitrogen atom in common and having a thiol substituent attached to a carbon atom of said diazine ring, or a salt of such compound. It also includes a photographic treating bath, such as a non-coupling developer containing at least one of such compounds or their salts, as well as the method of photographic development which includes developing a silver image in a silver halide emulsion in the presence of at least one of such compounds or their salts, for example with a developer containing at least one of such compounds or their salts. Such tetrazaindene compound is

most suitably one of the probable general Formulae VII and IX or of the general Formula XV.

The invention will be illustrated by, but is not limited to, the following examples:

EXAMPLE 1.—6-METHYL-1:3:3a:7-TETRAZAINDENE-4-THIOL

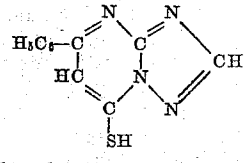


4-hydroxy-6-methyl-1:3:3a:7-tetrazaindene was prepared as described by Bülow et al. in "Berichte der deutschen chemischen Gesellschaft," 1909, vol. 42, 4638. 34 grams of this and 35 cc. of dimethylaniline were placed in a 1 liter round-bottomed flask and phosphorus oxychloride (100 cc.) added slowly. The flask was immersed in an oil bath at 125° and provided with a reflux condenser and calcium chloride tube. The solids dissolved slowly. After 1 hour the excess phosphorus oxychloride was removed on a steam bath at reduced pressure and the orange oil was poured into a water (1 liter). The tar dissolved on stirring to give a clear orange solution. This was extracted with chloroform until a sample on evaporation gave no crystalline residue. The chloroform extract was dried over anhydrous sodium sulfate and the solvent removed under reduced pressure at 50° C. The crystalline residue was dissolved in hot benzene (200 cc.) filtered from the orange residue and chilled. The crystals (24.5 gms.) together with a further 3.4 gms. obtained from the filtrate by adding petroleum ether (73% yield) formed flat yellow needles, M.P. 151° C., from benzene.

3.75 gms. of 4-chloro-6-methyl-1:3:3a:7-tetrazaindene prepared as described above, 1.7 gms. of thiourea and 20 cc. of methanol were refluxed together on a steam bath for 2–3 mins. The thiol separated rapidly. It (3.2 gms. 86.5%) formed orange yellow needles from water, decomposing at 278–279° C. with previous sublimation.

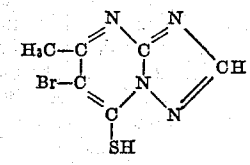
On dissolving it in hot 2 N-sodium carbonate solution and chilling the solution the sodium salt dihydrate crystallized as pale yellow needles. They are readily recrystallized from hot water and are suitable for use as an emulsion addendum. They soften at 180–190° C., resolidify and do not melt below 300° C.

EXAMPLE 2. — 6-PHENYL-1:3:3a:7-TETRAZAINDENE-4-THIOL



4-hydroxy-6-phenyl-1:3:3a:7-tetrazaindene (see British specification No. 619,557, Compound No. 5) (25 gms.), dimethylaniline (18.2 cc.) and phosphorus oxychloride (52 cc.) were heated together at 125° for 1 hour in an oil bath. The solvent was removed under reduced pressure and the residue treated with ice water. The brick-red solid was collected, dried and extracted with benzene. The benzene extract was concentrated to 50 cc., chilled and the solid, 6.7 gms., M.P. 158°, collected. This chloro-compound (8 gms.), thiourea (2.8 gms.) and methanol (30 cc.) were refluxed together for 3 mins. The required thiol separated rapidly. It was collected hot to give 7.9 gms., M.P. 282° C. It was dissolved in hot 2 N-aqueous sodium hydroxide (20 cc.), filtered and chilled to give a mass of yellow needles of the sodium salt hydrate. It was dissolved in ethanol (10 cc.). Almost immediately it crystallized in the anhydrous form as pale yellow needles, M.P. over 300° C.

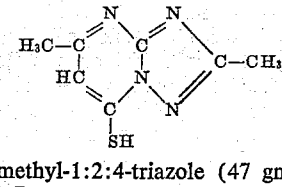
EXAMPLE 3.—5-BROMO-6-METHYL-1:3:3a:7-TETRAZAINDENE-4-THIOL



4-hydroxy-6-methyl-1:3:3a:7-tetrazaindene (15 gms.) was suspended in acetic acid (100 cc.) and treated at 20° C. with a solution of bromine (5.2 cc.) in acetic acid (20 cc.). The suspended crystals dissolved and the 5-bromo derivative crystallized. Water (250 cc.) was added and the crystals were collected. It (18 gms.) was dissolved in hot aqueous 0.2 N-sodium carbonate (1 liter) and acidified slowly with dilute hydrochloric acid. An excess of triethylamine was added to dissolve any unchanged starting material and the crystals were collected. From water it formed white needles, M.P. 269° C.

The bromo-derivative (22.9 gms.) was treated with dimethylaniline (15 cc.) and phosphorus oxychloride (75 cc.) at 125° C. for 1 hour. The solid only partly dissolved so phosphorus pentachloride (20.8 gms.) was then added and the heating continued for 2 hours. The solvents were removed by distillation and the residue treated with ice-water and extracted with chloroform. Removal of the dried chloroform left a black solid. Thiourea (8.0 gms.) and methanol (50 cc.) were added and the whole was refluxed for 5 minutes. A dark brown solid separated. It (15.3 gms.) was collected after cooling and dissolved in aqueous 2 N-sodium carbonate and boiled with active carbon. The hot solution was filtered, made up to 3/l. with hot water and gradually neutralized. Brown flocks first precipitated and were removed. On cooling 9.0 gms. (37%) yellow microcrystals, M.P. 215° C., were obtained analyzing correctly for the required thiol.

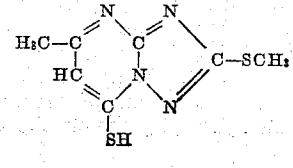
EXAMPLE 4. — 2:6-DIMETHYL-1:3:3a:7-TETRAZAINDENE-4-THIOL



3-amino-5-methyl-1:2:4-triazole (47 gms.), ethyl acetoacetate (65–7 gms.) and acetic acid (200 cc.) were refluxed together for 3 hours. The 4-hydroxy-2:6-dimethyl - 1:3:3a:7 - tetrazaindene separated on chilling. From water (charcoal) it (33 gms.) formed white needles, M.P. 307° C.

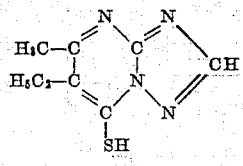
It (33 gms.) was treated at 125° C. for 1 hour with phosphorus oxychloride (90 cc.) and dimethylaniline (31.5 cc.) and the solvents were removed. The residue was treated with ice-water, filtered and the filtrate was extracted with chloroform. The dried chloroform was distilled off and the residual solid (20.4 gms., M.P. 148° C.) refluxed with thiourea (8.7 gms.) in methanol (100 cc.) for 3 minutes. The required thiol separated rapidly. It (17 gms.) was recrystallized from water to form yellow needles, M.P. 286° C. (decomp.).

EXAMPLE 5.—6 - METHYL - 2 - METHYLTHIO-1:3:3a:7-TETRAZAINDENE-4-THIOL



4 - hydroxy - 6 - methyl - 2 - methylthio - 1:3:3a:7-tetrazaindene (22 gms.), dimethylaniline (17.4 cc.) and phosphorus oxychloride (50 cc.) were heated together in an oil bath at 125° C. for 1 hour. The solvents were removed and the residue treated with ice-water and extracted with chloroform. The dried chloroform extract was distilled to remove solvent and the residue recrystallized from ethanol. It (11:5 gms.) (M.P. 113–116° C.), thiourea (4.1 gms.) and methanol (50 cc.) were heated together for 3 minutes on a steam bath. The thiol crystallized during this time. From ethanol it (5.3 gms.) formed light yellow crystals, M.P. 265° C.

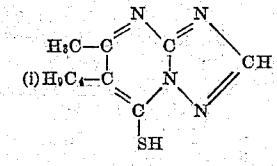
EXAMPLE 6. — 5-ETHYL-6-METHYL-1:3:3a:7-TETRAZAINDENE-4-THIOL



Ethyl ethylacetoacetate (100 gms.), 3-amino-1:2:4-triazole (50 gms.) and acetic acid (250 cc.) were refluxed for 3 hours, the solution was chilled and the crystals collected. The crystals had M.P. 275° C. and weight 49 gms. It is 5 - ethyl - 4 - hydroxy - 6 - methyl-1:3:3a:7-tetrazaindene. It (48 gms.), dimethylaniline (41.5 cc.) and phosphorus oxychloride (120 cc.) were heated in an oil bath at 125° C. for 1 hour. The solvent was distilled off and the residue after treatment with ice-water was taken up in chloroform, the solution was dried and the solvent distilled off. The residue (40.9 gms.) of chloro-compound formed yellow needles, M.P. 132° C., from ethanol.

It (40.9 gms.), thiourea (15.9 gms.) and methanol (150 cc.) were refluxed together for 3 minutes. The solid which separated (43 gms.) formed yellow needles, M.P. 270–273° C., from ethanol.

EXAMPLE 7. — 5-ISO-BUTYL-6-METHYL-1:3:3a:7-TETRAZAINDENE-4-THIOL

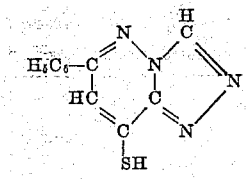


α-Iso-butylacetoacetic ester (0.1 mol.) and 5-amino-1:2:4-triazole (0.1 mol.) were refluxed together in glacial acetic acid (40 cc.) for 7 hours. On cooling the product was precipitated by the addition of water. It (5 - isobutyl - 4 - hydroxy - 6 - methyl - 1:3:3a:7 - tetrazaindene) was recrystallized from water as colorless needles, M.P. 258° C. (yield 60%).

The above (6 gms.), dimethyl aniline (6 gms.) and phosphorus oxychloride (18 gms.) were refluxed together at 125° C. for 4 hours, after which the excess oxychloride was removed under vacuum, and the residue poured onto crushed ice and extracted with chloroform. After drying, the solvent was removed and the resulting dark oil (5 gms.) (4-chloro-5-isobutyl-6-methyl-1:3:3a:7-tetrazaindene) used without further purification.

It (4 gms.) and thiourea (1.4 gms.) were refluxed together in ethanol for 2 hours during which time a yellow crystalline solid separated. After cooling the product was collected and washed while still on the filter with a small quantity of alcohol. It (3 gms.) was recrystallized from glacial acetic acid as small yellow crystals, M.P. 270° C. (dec.).

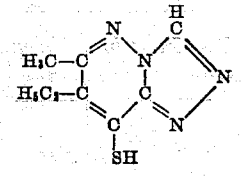
EXAMPLE 8. — 5-PHENYL-1:2:3a:4-TETRAZAINDENE-7-THIOL



Ethyl benzoylacetate (96 gms.) and 1-amino-1:3:4-triazole (42 gms.) were fused at 175–180° C. for 1 hour. Ethanol (25 cc.) was added to the orange melt to give a crystalline cake. It (21 gms.) formed cream needles, M.P. 284–285° C., from aqueous ethanol. It (20.8 gms.), dimethylaniline (15 cc.) and phosphorus oxychloride (55 cc.) were heated together in an oil bath at 125° C. for 1 hour. On removing the solvent the whole solidified. It was shaken with ice-water and chloroform and the dried chloroform layer evaporated to dryness. The solid was dissolved in benzene, filtered and the solution was chilled to give 12.8 gms. (56.5%) yield of chloro-compound. It formed straw-colored needles, M.P. 214° C.

The chloro-compound (10.9 gms.) was covered with a solution of potassium hydroxide (20 gms.) in water (200 cc.) which had been saturated with hydrogen sulfide. Ethanol (200 cc.) was then added and the whole brought to the boil. The solid dissolved and the filtered solution was then acidified with dilute hydrochloric acid. The pale yellow flocks which precipitated were recrystallized from ethanol. The required thiol (9.3 gms.) formed soft yellow needles, M.P. 173° C. (resolidified and then M.P. 250° C.).

EXAMPLE 9.—6 - ETHYL - 5 - METHYL - 1:2:3a:4-TETRAZAINDENE-7-THIOL



Ethyl ethylacetoacetate (74 gms.) and 1-amino-1:3:4-triazole (38.3 gms.) were heated at 170° C. in an oil bath for 1 hour. The temperature was then raised to 185° C. for a further 1 hour. The crumbly mass was boiled up with water, cooled and collected. It (48 gms.) formed colorless needles, M.P. 235° C., from ethanol. It is 7-hydroxy-6-ethyl-5-methyl-1:2:3a:4-tetrazaindene. It (40 gms.), dimethylaniline (33.6 cc.) and phosphorus oxychloride (112 cc.) were heated for 1 hour at 125° C. The solvent was distilled off at reduced pressure. The residue was decomposed with ice-water and chloroform. The aqueous phase was extracted with chloroform and the combined extracts dried and the solvent removed. The residual chloro-compound (colorless needles, M.P. 112° C., from ethanol) was then treated with potassium hydrogen sulfide as in Example 8. The required thiol formed glistening yellow plates, M.P. 238° C., from ethanol.

EXAMPLE 10.—5 - METHYL - 1:2:3a:4 - TETRAZAINDENE-7-THIOL

This was made as described by Bülow and Haas (loc. cit.), M.P. 218° C.

The following data will serve to illustrate the unique effects obtained when one of the mercapto compounds of my invention is incorporated in a photographic silver halide emulsion prior to coating on a conventional support. The data in the following tables were obtained by exposing the emulsions in the usual manner, followed by developing, fixing and washing. The resulting prints

were then hot-glazed in the usual manner. The following data were obtained:

Table A.—Silver chloride emulsion

[Compound incorporated at rate of 0.5 gm. per mol AgCl.]

Compound	Contrast	Maximum Density	
		Original	Hot glazed
None	1.4	1.65	1.41
Ex. 1		1.62	1.48
Ex. 2	2.8	1.61	1.60
Ex. 3		1.66	1.61
Ex. 6		1.61	1.60

Table B.—Silver bromide emulsion

[Compound incorporated at rate of 0.1 gm. per mol AgBr.]

Compound	Contrast	Maximum Density	
		Original	Hot glazed
None	2.8	1.81	1.56
Ex. 3		1.81	1.70
Ex. 4	3.1	1.81	1.69
Ex. 6	3.5	1.84	1.76

Table C.—Silver chloride emulsion

[Compound incorporated at rate of 0.5 gm. per mol AgCl.]

Compound	Contrast	Maximum Density	
		Original	Hot glazed
None	5.7	1.53	1.35
Ex. 10	7.6	1.63	1.62

Table D.—Silver bromide emulsion

[Compound incorporated at rate of 0.5 gm. per mol AgBr.]

Compound	Contrast	Maximum Density	
		Original	Hot glazed
None	1.73	1.67	1.56
Ex. 10	1.80	1.68	1.64

Table E.—Silver chloride emulsion

[Compound incorporated at rate of 1.0 gm. per mol AgCl.]

Compound	Contrast	Maximum Density	
		Original	Hot glazed
None	8.8	1.75	1.59
Ex. 8	8.8	1.75	1.70

Table F.—Silver bromide emulsion

[Compound incorporated at rate of 0.1 gm. per mol AgBr.]

Compound	Contrast	Maximum Density	
		Original	Hot glazed
None	2.6	1.81	1.56
Ex. 9	3.5	1.84	1.76

The data in the following table were obtained by treating an exposed ordinary X-ray emulsion (such as a silver bromiodide emulsion) with an aqueous sodium carbonate solution containing one of the compounds prepared in the examples, the concentration of the tetrazaindene compound being given in the table. After treatment of the exposed emulsion with the aqueous alkaline solution, it was developed in the usual manner.

Table G.—Pretreatment of X-ray emulsion

Compound	Concentration (percent) in 1% aqueous sodium carbonate	Maximum Density		
		Reflection	Transmission	
			Wet	Dry
None		1.21	1.63	1.56
Ex. 1	0.01	1.46	1.91	1.67
Ex. 2	0.1	1.51	1.79	1.57
Ex. 3	0.1	1.44	1.76	
Ex. 4	0.1	1.51	1.70	
Ex. 5	0.1	1.42	1.71	
Ex. 6	0.1	1.45	1.75	
Ex. 7	0.1	1.42	1.70	

As indicated above, many of the tetrazaindene compounds of my invention are useful in stabilizing photographic silver halide emulsions, and in particular, high-speed negative emulsions. The amount of tetrazaindene compound required to stabilize the emulsion can be determined in the usual manner by incorporating varying amounts of stabilizer in a series of emulsions. The test strips can then be stored under conditions of constant temperature and humidity, before the test strips are exposed and developed. In general, storage for a period of about two weeks at 120° F. is sufficient to accelerate the formation of fog.

In the following table, the antifoggant and stabilizing action were determined by incubation of the emulsion for two weeks at a temperature of 120° F. and constant relative humidity (obtained by placing the emulsions in closed containers, the room temperature being about 70° F. and relative humidity about 55% prior to sealing the containers).

The efficiency of the various antifoggants was determined by measuring the speed, gamma and fog of the incubated emulsions containing an antifoggant and comparing these measurements with those of the same batch of emulsion before incubation. Also, similar measurements were made with a photographic emulsion containing no antifoggant, both before and after incubation.

The tests were made using high speed, negative-type silver bromiodide emulsions (coated on cellulose acetate supports), which had been panchromatically sensitized with a cyanine dye and chemically sensitized with silver and gold compounds.

The test films were exposed for $\frac{1}{25}$ second on an intensity scale sensitometer (Eastman Ib type) and developed for five minutes in a developer having the following composition:

	Grams
N-methyl-p-aminophenol sulfate	2.5
Hydroquinone	2.5
Sodium sulfite (desiccated)	30.0
Sodium metaborate	10.0
Potassium bromide	0.5
Water to make 1 liter.	

The speed, gamma and fog for each of the emulsion coatings were then measured as indicated above. The speed figure (CR) shown in the following table is on a logarithmic scale, obtained by the formula:

$$100 \text{ (1 minus log } E\text{)}$$

where E is the exposure in meter-candle-seconds of sunlight quantity required to produce a density of 0.30 above fog. The results obtained are given in the following table.

Table H

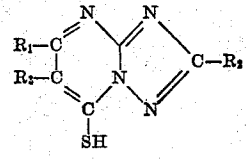
Addenda—Compound	g./mol. AgX	Fresh Coatings			Incubated 2 Weeks, 120° F.		
		CR Speed	γ	Fog	Speed	γ	Fog
None		304	1.33	.13	272	0.84	.50
		306	1.20	.13	279	.80	.45
Ex. 10	.03	294	1.37	.11	284	.94	.32
Ex. 8	.03	289	1.31	.12	289	1.06	.17
Ex. 9	.15	302	1.30	.15	286	.91	.35
Ex. 1	.03	294	1.26	.14	289	.98	.20
Ex. 3	.03	296	1.25	.12	288	.96	.19
Ex. 6	.03	292	1.13	.11	286	.97	.17
Ex. 5	.03	303	1.20	.14	289	.89	.25
Ex. 4	.15	297	1.03	.15	280	.86	.17

When using the compounds of my invention for the purpose of stabilizing photographic silver halide emulsions in accordance with the above directions, it is convenient to employ from about 5 to 100 mg. per mol. of silver halide in the emulsion.

The term "thiol" or mercapto as used in the foregoing specification and the following claims is intended to mean not only —SH, but also water-soluble salts thereof, such as sodium, potassium, ammonium, organic ammonium, etc. salts.

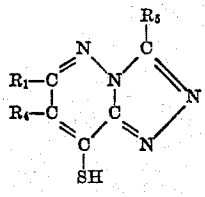
What I claim as my invention and desire secured by Letters Patent of the United States is:

1. The method of preventing image degradation of an exposed silver halide emulsion during processing which comprises performing at least one of the steps of developing, fixing, washing and drying said emulsion in the presence of a compound selected from those represented by the following general formula:



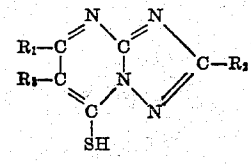
wherein R_1 represents a member selected from the group consisting of an alkyl group containing from 1 to 4 carbon atoms, an aralkyl group containing from 7 to 8 carbon atoms, and a mononuclear aromatic group of the benzene series, R_2 represents a member selected from the group consisting of a hydrogen atom, an alkyl group containing from 1 to 4 carbon atoms, an aralkyl group containing from 7 to 8 carbon atoms, a mononuclear aromatic group of the benzene series, an alkylthio group containing from 1 to 2 carbon atoms, an aralkylthio group, and an arylthio group containing from 6 to 7 carbon atoms, and R_3 represents a member selected from the group consisting of a hydrogen atom, a halogen atom and an alkyl group.

2. The method of preventing image degradation of an exposed silver halide emulsion during processing which comprises performing at least one of the steps of developing, fixing, washing and drying said emulsion in the presence of a compound selected from those represented by the following general formula:



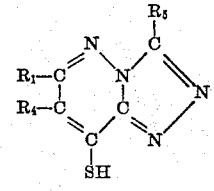
wherein R_1 represents a member selected from the group consisting of an alkyl group containing from 1 to 4 carbon atoms, an aralkyl group containing from 7 to 8 carbon atoms, and a mononuclear aromatic group of the benzene series, R_4 represents a member selected from the group consisting of a hydrogen atom and an alkyl group containing from 1 to 4 carbon atoms, and R_5 represents a member selected from the group consisting of a hydrogen atom, an alkyl group containing from 1 to 4 carbon atoms, an aralkyl group containing from 7 to 8 carbon atoms, a mononuclear aromatic group of the benzene series, an alkylthio group containing from 1 to 2 carbon atoms, an aralkylthio group, and an arylthio group containing from 6 to 7 carbon atoms.

3. The method of preventing image degradation of an exposed silver halide emulsion during processing which comprises incorporating in at least one of the developing, fixing and washing baths used to process said emulsion, a compound selected from those represented by the following general formula:



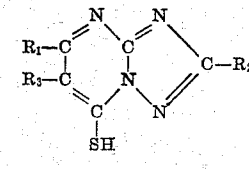
wherein R_1 represents a member selected from the group consisting of an alkyl group containing from 1 to 4 carbon atoms, an aralkyl group containing from 7 to 8 carbon atoms, and a mononuclear aromatic group of the benzene series, R_2 represents a member selected from the group consisting of a hydrogen atom, an alkyl group containing from 1 to 4 carbon atoms, an aralkyl group containing from 7 to 8 carbon atoms, a mononuclear aromatic group of the benzene series, an alkylthio group containing from 1 to 2 carbon atoms, an aralkylthio group, and an arylthio group containing from 6 to 7 carbon atoms, and R_3 represents a member selected from the group consisting of a hydrogen atom, a halogen atom and an alkyl group.

4. The method of preventing image degradation of an exposed silver halide emulsion during processing which comprises incorporating in at least one of the developing, fixing and washing baths used to process said emulsion, a compound selected from those represented by the following general formula:



wherein R_1 represents a member selected from the group consisting of an alkyl group containing from 1 to 4 carbon atoms, an aralkyl group containing from 7 to 8 carbon atoms, and a mononuclear aromatic group of the benzene series, R_4 represents a member selected from the group consisting of a hydrogen atom and an alkyl group containing from 1 to 4 carbon atoms, and R_5 represents a member selected from the group consisting of a hydrogen atom, an alkyl group containing from 1 to 4 carbon atoms, an aralkyl group containing from 7 to 8 carbon atoms, a mononuclear aromatic group of the benzene series, an alkylthio group containing from 1 to 2 carbon atoms, an aralkylthio group, and an arylthio group containing from 6 to 7 carbon atoms.

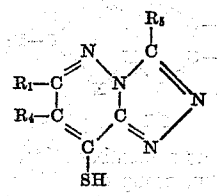
5. A photographic silver halide emulsion containing a compound selected from those represented by the following general formula:



wherein R_1 represents a member selected from the group consisting of an alkyl group containing from 1 to 4 carbon

atoms, an aralkyl group containing from 7 to 8 carbon atoms, and a mononuclear aromatic group of the benzene series, R_2 represents a member selected from the group consisting of a hydrogen atom, an alkyl group containing from 1 to 4 carbon atoms, an aralkyl group containing from 7 to 8 carbon atoms, a mononuclear aromatic group of the benzene series, an alkylthio group containing from 1 to 2 carbon atoms, an aralkylthio group, an an arylthio group containing from 6 to 7 carbon atoms, and R_3 represents a member selected from the group consisting of a hydrogen atom, a halogen atom and an alkyl group.

6. A photographic silver halide emulsion containing a compound selected from those represented by the following general formula:



wherein R_1 represents a member selected from the group consisting of an alkyl group containing from 1 to 4 carbon atoms, an aralkyl group containing from 7 to 8 carbon atoms, and a mononuclear aromatic group of the

benzene series, R_4 represents a member selected from the group consisting of a hydrogen atom and an alkyl group containing from 1 to 4 carbon atoms, and R_5 represents a member selected from the group consisting of a hydrogen atom, an alkyl group containing from 1 to 4 carbon atoms, an aralkyl group containing from 7 to 8 carbon atoms, a mononuclear aromatic group of the benzene series, an alkylthio group containing from 1 to 2 carbon atoms, an aralkylthio group, and an arylthio group containing from 6 to 7 carbon atoms.

7. A photographic silver halide developing-out emulsion containing 6-methyl-1:3:3a:7-tetrazaindene-4-thiol.

8. A photographic silver halide developing-out emulsion containing 5-bromo-6-methyl-1:3:3a:7-tetrazaindene-4-thiol.

9. A photographic silver halide developing-out emulsion containing 2:6-dimethyl-1:3:3a:7-tetrazaindene-4-thiol.

10. A photographic silver halide developing-out emulsion containing 5-ethyl-6-methyl-1:3-3a:7-tetrazaindene-4-thiol.

11. A photographic silver halide developing-out emulsion containing 2-phenyl-1:2:3a:4-tetrazaindene-7-thiol.

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