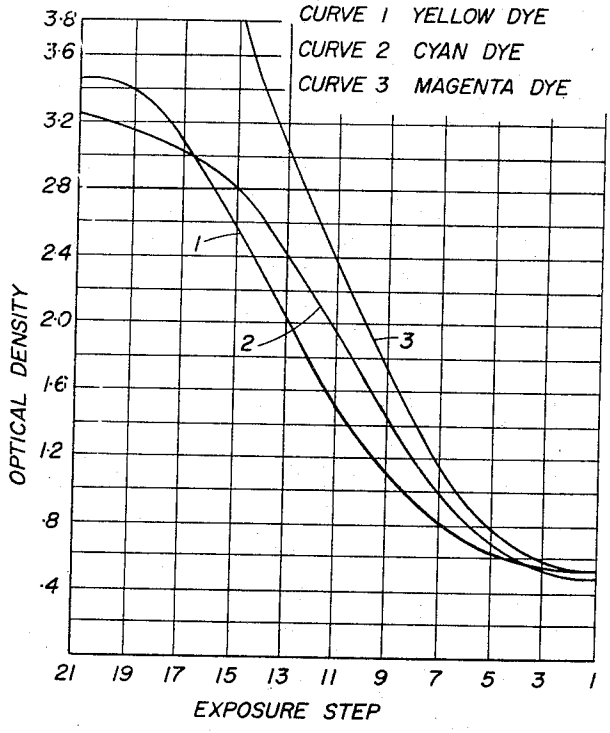
April 2, 1968 J. R. ABBOTT ETAL 3,376,310

SUBSTITUTED 1-PHENYL-5-MERCAPTOTETRAZOLES

Original Filed Sept. 1, 1964

FIG. 1



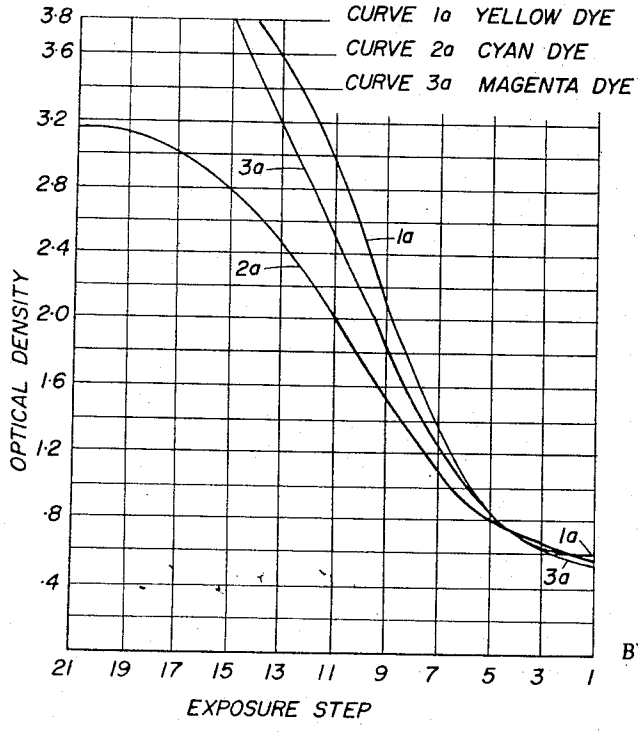


FIG. 2

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United States Patent Office 3,376,310 Patented Apr. 2, 1968

3,376,310

SUBSTITUTED 1-PHENYL-5-MERCAPTO-TETRAZOLES

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Original application Sept. 1, 1964, Ser. No. 393,639, now Patent No. 3,295,976, dated Jan. 3, 1967. Divided and this application May 16, 1966, Ser. No. 565,365

10 Claims. (Cl. 260—308)

ABSTRACT OF THE DISCLOSURE

1-phenyl-5-mercaptotetrazoles which have a substituted sulfonamido group or a substituted acylamido group attached to the 1-phenyl group are used advantageously in compositions that are applied to photographic material during photographic processing prior to the development step, the development inhibiting affect produced by the immediate substituted 1-phenyl-5-mercaptotetrazoles being such that when compositions containing them are applied to multilayer color elements during processing prior to development, overdevelopment of the top (outermost layer) will be prevented even at temperatures up to about 160° F.

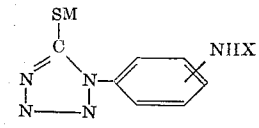
This is a divisional application of U.S. patent application Ser. No. 393,639, filed Sept. 1, 1964, now U.S. Patent 3,295,976, granted Jan. 3, 1967.

The present invention relates to novel compounds useful in chemical reactions involved in the processing of color film. More particularly, the present invention relates to compounds capable of selectively preventing negative overdevelopment.

In multi-layer photographic elements there are usually three differently sensitive emulsion layers coated on one side of a single support. These emulsion layers may contain color couplers, such as described in U.S. Patent 2,322,027, issued to E. E. Jelley and P. W. Vittum on June 15, 1943, which are capable of reacting with the development product of aromatic amino developing agents on photographic development to form colored images. One of the difficulties encountered in the development of such multi-layer elements, especially when the development is carried out at high temperatures, is the overdevelopment of the top emulsion layer, normally the blue sensitive, yellow-image forming layer, before the bottom layer is fully developed. The overdevelopement, which is caused primarily by the excessive concentration of the developer in the top layer, results in improper image density in that layer as compared to the remaining layers. Although it had been known that certain compounds could be employed to inhibit the overdevelopment of the top layer of color photographic elements, these compounds suffered from the disadvantage, although diffusing slower than the developer, of penetrating beyond the top sensitive emulsion layer and adversely affecting the image density in the next layers.

It is therefore an object of the present invention to provide a novel class of compounds. It is another object of the present invention to provide a novel class of compounds which act as inhibitors in the development of the top layer of multi-layer photographic element without affecting the other layers in the element. A further object of the present invention is to provide a class of compounds which aid in the development of color images of uniform characteristics in a multi-layer photographic element. A still further object is to provide a method for permitting high temperature development of multi-layer color elements. Other objects will be apparent hereinafter.

In accordance with the present invention it was discovered that 5-mercaptotetrazoles having the general formula



Formula I

wherein M is a member of the class consisting of alkali metals and hydrogen and X is a radical having a formula selected from the group consisting of —SO_2R and —COR, wherein R is a hydrocarbyl radical of 1 to 22 carbon atoms, act as selective inhibitors in the development of multi-layer photographic elements. The hydrocarbyl radical "R" in the novel 5-mercaptotetrazoles may be an alkyl group, an aryl group, an alkaryl group, an aralkyl group, or an alkaralkyl group. The hydrocarbyl group may further contain substitutents such as alkoxy, phenoxy, halogen, cyano, nitro, amino, substituted amino, sulfo, sulfamyl, substituted sulfamyl, sulfonylphenyl, sulfonylalkyl, fluosulfonyl, sulfonamidophenyl, sulfonamidoalkyl, carboxylic acid, carboxylate, carbamyl, carbamylphenyl, carbamylalkyl, carbonylalkyl, carbonylphenyl and similar groups. It is to be understood that the term "hydrocarbyl" as employed in the present invention is used as including the aforesaid and similar substituent groups. Many of the aforesaid functional substituents are useful in increasing the solubility of the novel mercaptotetrazole.

The location of the —NHX group on the phenyl ring of the 1-phenyl-5-merceptotetrazole is not critical and may be ortho, para, or meta.

The novel compounds are produced by the reactions of the 1-(aminophenyl)-5-mercaptotetrazole hydrochloride with an acid chloride having the formu'a RCOCl where "R" has the above indicated meaning. The 1-(aminophenyl)-5-mercaptotetrazole is prepared by reaction of an aminoacetanilide, (ortho-, meta-, or para-), with thiophosgene to result in the formation of the corresponding acetamidophenyl isothiocyanate which is then reacted with an azide to form the mercaptotetrazole ring. This product is then hydrolyzed with concentrated hydrochloric acid to form the 1-(aminophenyl)-5-mercaptotetrazole hydrochloride. The formation of the mercaptotetrazole ring has been described by Stolle and Strittmatter in the Journal fur Praktische Chemie, vol. 133, pages 60 to 64 and by Stolle and Fr. Henke-Stark in the same journal vol. 124, pages 261–300. An alternate method for the production of the substituted phenyl-5-mercaptotetrazole is to react an acetamidophenyl substituted thiosemicarbazide with nitrous acid as described by Freund and Hempel in Berichte der Deutschen Chemischen Gesellsdraft, vol. 28 at page 77.

Acid chlorides which may be employed in the reaction with the mercaptotetrazole hydrochloride include the chlorides of the following acids: acetic, aceto-acetic, difluoroacetic, propionic, valeric, iso-valeric, caproic, caprylic, undecanoic, stearic, benzoic, o-acetoxybenzoic, anthranilic, 3-amino-6-nitrobenzoic, p-tolyl acetic, 2,4-dinitrophenyl-acetic, methylsulfonic, o-toluene sulfonic, benzene sulfonic, p-bromobenzene sulfonic and o-formylbenzene sulfonic acid.

The compounds of the present invention are used in connection with the color processing of multi-layer photographic elements such as described in the Jelley and Vittum patent U.S. 2,322,027. The sensitive elements in that type of photographic element comprise a support of cellulose ester, paper or other suitable base having coated thereon a red sensitive emulsion layer containing a cyan-forming coupler, a green sensitive emulsion layer containing a magenta-forming coupler and a blue sensitive emulsion layer containing a yellow-forming coupler. The couplers may be of the composition and incorporated in

the manner described in the said Jelley and Vittum patent.

The compounds of the present invention are however not limited in their use to the described multi-layer element. Thus, the photographic element may contain fewer or more sensitive emulsion layers and may also contain filter interlayers, subbing layers, backing layers and overcoating layers applied in the well known manner. One or more of the emulsion layers may also be free of incorporated couplers, the coupler or couplers for these layers being contained in the color developing solution.

One of the advantages of the compounds of the present invention when employed as overdevelopment inhibitors is their use in high temperature processing. Thus, photographic elements may be developed at temperatures of 140° to 160° F. when using the compounds of the present invention.

In one embodiment of the present invention the 1-(aminophenyl)-5-mercaptotetrazole is applied during processing to the image-exposed multi-layer color photographic element so that this compound is present in the top silver halide emulsion layer (but not in the middle or bottom layers) during the negative development step of the color process. This is advantageously accomplished by including the 5-mercaptotetrazole of Formula I in the prehardener solution, in the hydroxylamine sulfate bath following the prehardener or in the negative developer solution or in combinations of these. The compounds of Formula I are used over a wide range of concentrations, i.e., from about 0.001 g./l. to about 1 g./l. The optimum amount will depend upon many factors, such as, the particular compound of Formula I, the processing solution compositions, developer activities, processing temperature, the characteristics of the multi-layer color element and others. The optimum amount of our compound of Formula I for use according to our invention can be readily determined by methods well known in the art.

The prehardener solution used according to our invention comprises formaldehyde, and a compound of Formula I. Succinaldehyde is used to advantage in our prehardener solutions.

The present invention is further illustrated by the following examples:

Example I

A solution of 18.7 g. (0.1 mole) of m-aminoacetanilide hydrochloride in 100 ml. of water was added to a suspension of 25 g. (0.22 mole) of thiophosgene in 100 ml. of water. The solid isothiocyanate was collected by filtration and air dried.

This solid, 19.5 g. (0.25 mole) of sodium azide and 50 ml. of ethanol were added to 500 ml. of water. The solution was refluxed for three hours, cooled and acidified with concentrated hydrochloric acid. The resulting solid 5-mercaptotetrazole was collected and dried.

This product was suspended in 500 ml. of a 50–50 water, concentrated hydrochloric acid mixture and boiled until complete solution was obtained. On cooling white needles separated out and were collected. The product was identified as the 1-(3-aminophenyl)-5-mercaptotetrazole hydrochloride.

To a suspension of 2.3 g. (0.01 mole) of 1-(3-aminophenyl)-5-mercaptotetrazole hydrochloride in 20 ml. of acetonitrile, 1:6 g. (0.02 mole) of pyridine was added. To the resulting solution, 0.78 g. (0.01 mole) of acetyl chloride was added and the mixture was heated at 60° C. for one hour. The temperature was then raised to boiling and water was added until clouding occurred. On cooling the solid 1-(3-acetamido)phenyl - 5 - mercaptotetrazole, M.P. 201–2° C., precipitated out of the mixture and was isolated by filtration and then dried.

Example II

Employing the procedure of Example I, 1-(3-caproamido)phenyl-5-mercaptotetrazole, M.P. 188–9° C., was prepared from the 1-(3-aminophenyl)-5-mercaptotetrazole hydrochloride by reaction with caproyl chloride.

Example III

Employing the procedure of Example I, 1-(3-pelargonamido)phenyl-5-mercaptotetrazole, M.P. 172–3° C. was prepared from the 1-(3-aminophenyl)-5-mercaptotetrazole hydrochloride by reaction with pelargonyl chloride.

Example IV

Employing the procedure of Example I, 1-{3-[alpha-(2,4-di-t-amylphenoxy)acetamido]phenyl} - 5 - mercaptotetrazole, M.P. 164–6° C. was prepared from the 1-(3-aminophenyl)-5-mercaptotetrazole hydrochloride by reaction with alpha-(2,4-di-t-amylphenoxy)acetyl chloride.

Example V

Employing the procedure of Example I, 1-(3-methyl sulfonamido)phenyl-5-mercaptotetrazole, M.P. 163° C. (dec.), was prepared from the 1-(3-aminophenyl)-5-mercaptotetrazole hydrochloride by reaction with methyl sulfonyl chloride.

Example VI

Employing the procedure of Example I, 1-(3-p-toluene sulfonamido)phenyl-5-mercaptotetrazole, M.P. 140–3° C. was prepared from the 1-(3-aminophenyl)-5-mercaptotetrazole hydrochloride by reaction with p-toluene sulfonyl chloride.

The foregoing examples have illustrated one of the preparative methods employed to produce the novel compounds of the present invention. It will be apparent that the same method can be employed using the other acid chlorides described hereinabove, as well as any other acid chloride which is within the scope of the definition of the novel compounds of the present invention.

The use of the compounds of the present invention is further illustrated in the following example:

Example VII

Two strips of a multi-layer color element comprising a support coated with a red-sensitive silver halide emulsion layer containing a cyan-forming coupler, a green-sensitive silver halide emulsion layer containing a magenta-forming coupler, a bleachable yellow filter layer and a blue-sensitive silver halide emulsion layer containing a yellow-forming coupler were given identical exposures to a neutral density step wedge on an Eastman 1B sensitometer, then given color processing as follows:

Solution:	Time in seconds
Prehardener	6
Hydroxylamine sulfate	15
Negative developer	35
Stop bath	10
Re-exposure to #2 photoflood (30 sec. front and 30 sec. back).	
Color developer	60
Stop bath	20
Wash	20
Bleach	60
Fix	30
Wash	30
Stabilizer	15
Dry	15

The prehardener solution was a formalin-succinaldehyde prehardener such as is described in Baden et al, U.S. Ser. 321,323 filed Nov. 4, 1963, now Patent No. 3,294,536. A hydroxylamine sulfate neutralizer bath such as is described by Blackmer and Vogt in U.S. Ser. 111,489 filed May 22, 1961, now Patent No. 3,168,400 was used. A conventional silver halide solvent type hydroquinone—p-methylaminophenol sulfate developer was used for negative development. A conventional p-phenylenediamine color developer solution was used for color development. The stop bath was a conventional

acetic acid type, the bleach a conventional alkali metal ferricyanide bromide type, the fixing bath a conventional alkali metal thiosulfate bath, and the stabilizer a solution of formalin and commercially available "Photo-Flo." The solutions were used at 160° F. in a drum processor. The two strips were given identical processing except for the prehardener solution. Strip No. 1 was given standard prehardener solution, while Strip No. 2 was given standard prehardener solution to which 0.02 g./l. of 1-(3-caproamidophenyl)-5-mercaptotetrazole has been added. Optical density measurements were made of the yellow dye, the cyan dye and the magenta dye in the image of each stop of the neutral density tablet in each strip. The accompanying drawings, FIGS. 1 and 2, show graphs of these data. FIG. 1 shows for Strip 1 which was given standard prehardening, the density curves **1**, **2**, and **3** for yellow dye, cyan dye and magenta dye respectively. FIG. 2 shows for Strip 2 which was prehardened with the prehardener containing 1-(3-caproamidophenyl)-5-mercaptotetrazole, the density curves **1***a*, **2***a*, and **3***a* for yellow dye, cyan dye and magenta dye respectively.

FIG. 1 shows that the yellow dye densities are too low with respect to the cyan and magenta dye densities at almost every step and color reproduction is unsatisfactory. FIG. 2 shows that the yellow dye densities in Strip No. 2 are good and their relationship to the cyan and magenta dye densities will give good color reproduction. A comparision of FIG. 1 with FIG. 2 shows that curve **1***a* (yellow dye) is 50% higher at step **6**, 78% higher at step **8**, and 84% higher at step **12** than curve **1** at the same steps respectively, while curve **2** is substantially the same as curve **2***a* and curve **3** is substantially the same as curve **3***a*. This shows that the 1-(3-caproamidophenyl)-5-mercaptotetrazole in the prehardener reduced the negative development in the top yellow-forming layer but had virtually no effect on the negative development of the other image layers. One would expect that the substantial inhibiting effect produced by the 1-(3-caproamidophenyl)-5-mercaptotetrazole on the developing action of the relatively strong negative developer would be much greater on the relatively weak color developer in the yellow-forming layer thus resulting in the development of little or no yellow dye. It is therefore very unexpected that Strip No. 2 would have from 50 to 84% more yellow dye developed than Strip No. 1.

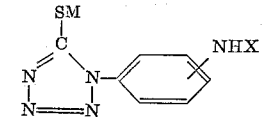
Similar results are obtained by repeating Example VII but using other 5-mercaptotetrazoles of formula I in the prehardener solution in place of 1-(3-caproamidophenyl)-5-mercaptotetrazole.

Alternatively the 5-mercaptotetrazoles of formula I are used to advantage in the hydroxylamine sulfate bath or in the negative developer solution to inhibit the negative development of only the top layer of the multilayer photographic element so that the top layer is not overdeveloped relative to the middle and bottom image-forming layers by the high temperature negative developer solution.

It will be understood that the modifications and examples included in the present specification are illustrative only and that the invention described is to be taken as limited only by the scope of the appended claims.

What is claimed is:

1. A mercaptotetrazole of the formula:

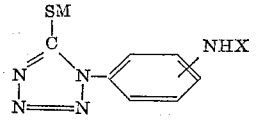


wherein M is a member of the class consisting of alkali metals and hydrogen, and X is a radical having a formula selected from the class consisting of —SO_2R and —COR wherein R is a radical containing from 1 to 22 carbon atoms selected from the class consisting of alkyl, alkoxyalkyl, phenoxyalkyl, halogen substituted alkyl, nitroalkyl, phenyl, alkoxyphenyl, phenoxyphenyl, halogen substituted phenyl, nitrophenyl, alkphenyl, alkoxyalkphenyl, phenoxyalkphenyl, halogen substituted alkphenyl, nitroalkphenyl, phenylalkyl, alkoxyphenylalkyl, phenoxyphenylalkyl, halogen substituted phenylalkyl, nitrophenylalkyl, alkphenylalkyl, alkoxyalkphenylalkyl, phenoxyalkphenylalkyl, halogen substituted alkphenylalkyl, nitroalkphenylalkyl and alkphenoxyalkyl.

2. A mercaptotetrazole of claim **2** in which X represents a radical having the formula —SO_2R.

3. A mercaptotetrazole of claim **2** in which X represents a radical having the formula —COR.

4. A mercaptotetrazole having the formula:



wherein M is a member of the class consisting of alkali metals and hydrogen and X is a radical having a formula selected from the class consisting of —SO_2R and —COR wherein R is a radical selected from the class consisting of alkyl of from 1 to 22 carbon atoms, alkylphenoxyalkyl of 8 to 22 carbon atoms, phenyl, and alkylphenyl having from 7 to 22 carbon atoms.

5. 1-(3-acetamido)phenyl-5-mercaptotetrazole.

6. 1-(3-caproamido)phenyl-5-mercaptotetrazole.

7. 1-(3-pelargonamido)phenyl-5-mercaptotetrazole.

8. 1 - {3 - [alpha - (2,4-di-t-amylphenoxy)acetamido] phenyl}-5-mercaptotetrazole.

9. 1 - (3 - methylsulfonamido)phenyl-5-mercaptotetrazole.

10. 1 - (3 - p - toluenesulfonamido)phenyl - 5-mercaptoterazole.

References Cited

UNITED STATES PATENTS

2,386,869 10/1945 Kendall ---------- 260—308

ALTON D. ROLLINS, *Primary Examiner.*

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,376,310 Dated April 2, 1968

Inventor(s) John R. Abbott and Ilmari F. Salminen

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 6, line 25 (first line of Claim 2) between "claim" and "in", delete "2" and substitute therefor --1--; and line 27 (first line of Claim 3) between "claim" and "in", delete "2" and substitute therefor --1--.

SIGNED AND
SEALED
DEC 23 1969

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

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Commissioner of Patents