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MERCAPTO HETEROCYCLIC ADDENDA FOR REVERSAL COLOR DEVELOPMENT

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19 Claims. (Cl. 96—22)

This invention relates to color photography, and more particularly, to a method of processing multi-layer color films or papers in such a manner as to reduce color fog and give maximum color density.

In multi-layer photographic elements used for color photography, there are usually three selectively sensitive emulsion layers coated on one side of a single support. For example, the uppermost layer is generally blue-sensitive, the next layer is generally green-sensitive, while the emulsion layer adjacent the support is generally red-sensitive. Between the blue-sensitive and green-sensitive layers is a filter layer for absorbing blue radiation which may be transmitted through the blue-sensitive layer. The multi-layer coating can also have other interlayers for specialized purposes. Such multi-layer materials have been previously described in the prior art, such as Mannes et al. U.S. Patent 2,252,718, issued August 19, 1941. Other arrangements of the sensitive layers are also known.

Color materials of the type employed in the instant invention are those intended primarily for reversal processes, wherein the exposed material is given a conventional black-and-white development, followed by a reversal exposure, or exposures, and color development.

The color materials used in my invention comprise emulsions which can contain color-forming materials or couplers, or these color couplers can be used instead in the color developers.

It is, therefore, an object of my invention to provide improved developers for reversal color photography. Another object is to provide a method of inhibiting color fog and increasing the maximum color density. Other objects will become apparent from a consideration of the following examples and description.

During the black-and-white development of multi-layer color materials, fog centers are introduced into the unexposed regions, and upon reversal exposure and subsequent color development, these unexposed areas have deposited therein coupled color-forming materials, resulting in severe loss of color quality. For example, in processing color materials of the Kodachrome type, color developer containing a cyan coupler results not only in development of the red-sensitive layer, but also in development of cyan fog in the blue- and green-sensitive layers. This fog is particularly severe in emulsions which contain conventional chemical sensitizers, such as gold sensitizers, sulfur sensitizers, etc., or polyethyleneglycol type sensitizers.

I have now found that such undesirable fog can be eliminated or materially reduced by adding a heterocyclic compound containing a mercapto (SH) group to one or more of the color developers. These heterocyclic compounds decrease color fog in the unexposed areas with no substantial loss of color density in the exposed areas. These compounds can be conveniently added to the color developer, which may or may not contain a color coupler or color-forming compound, depending upon the particular color material being processed. It is to be understood that my invention comprises the use of color materials which may contain the color couplers or color-forming compounds either in the emulsions or in the color developing solutions. Particular benefits have been obtained with color materials wherein the color couplers or color-forming materials are present in the color developing solutions.

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It is known that a colored image can be formed by adding to certain color developing solutions, or by incorporating in the silver halide emulsion, a compound which couples during development with the oxidation product of the developing agent, thus forming a colored compound which is deposited adjacent to the silver grains of the silver image during such development. Such compound which is employed in conjunction with the developing agent for the silver and which couples with the oxidation product of the developing agent during development is referred to as a color-forming compound or coupler. Such compounds usually belong to one of three widely known types, i.e., pyrazolone couplers, phenol couplers, or open-chain ketomethylene couplers. These couplers produce, respectively, magenta, cyan and yellow images.

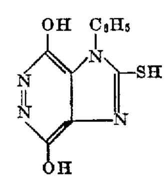
The heterocyclic compounds useful in practicing my invention include tetrazaindenyl and pentazaindenyl compounds containing a free mercapto (SH) group or an alkali metal salt thereof (e.g., sodium, potassium, etc.). These heterocyclic compounds can advantageously be represented by the following general formula:

$$R—(CH_2)_{n-1}—SM$$

wherein R represents a tetrazaindenyl or pentazaindenyl group, *n* represents a positive integer of from 1 to 2, and M represents a hydrogen atom or an alkali metal atom (e.g., sodium, potassium, etc.).

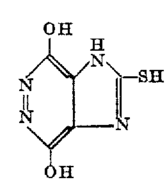
Typical heterocyclic compounds include, for example, the following:

(1)



4,7-dihydroxy-2-mercapto-1-phenyl-1,3,5,6-tetrazaindene

(2)



4,7-dihydroxy-2-mercapto-1,3,5,6-tetrazaindene

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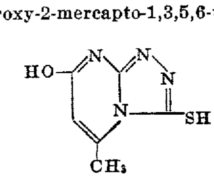

6-hydroxy-3-mercapto-4-methyl-1,2,3a,7-tetrazaindene

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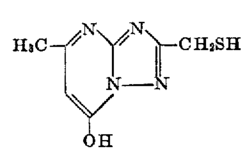
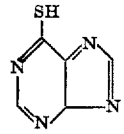


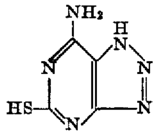
4-hydroxy-2-mercaptomethyl-6-methyl-1,3,3a,7-tetrazaindene

(5)



7-mercapto-1,3,4,6-tetrazaindene

(6)



7-amino-5-mercapto-1,2,3,4,6-pentazaindene

Many of the heterocyclic compounds useful in practicing my invention have been previously described in the prior art. See, for example, Allen et al. U.S. Patent 2,743,181, dated April 24, 1956; I.C.I. British Patent 701,054, published December 16, 1953; Parker et al. U.S. Patent 2,543,333, dated February 27, 1951; Fry U.S. Patent 2,566,659, dated September 4, 1951; etc.

The heterocyclic compounds employed in the color developers of my invention can be utilized in various concentrations depending upon the particular emulsions employed, the concentration of silver halides in the emulsions, and the concentration of the developing agents in the developers. In general, not less than about 5 mg. per liter of developer of heterocyclic compound should be employed. The most advantageous concentration can be determined by developing a series of test strips of silver halide emulsions wherein the concentration of heterocyclic compound is varied, as well as the concentration of the developing agent. The usual addenda can be employed in the developers, such as strongly alkaline agents, sodium carbonate, potassium carbonate, sodium hydroxide, etc, restraining agents, such as potassium bromide, stain preventives, such as alkali metal sulfites, etc.

My invention is primarily directed to the development of the ordinarily employed gelatino-silver-halide developing-out emulsions, e.g., gelatino-silver-chloride, -chlorobromide, -chloroiodide, -chlorobromiodide, -bromide and -bromiodide developing-out emulsions. While the results in the following examples were obtained using gelatino-silver-bromiodide emulsions, excellent results can also be obtained using other silver halide emulsions. These emulsions can be coated in the usual manner on any suitable support, e.g., glass, cellulose nitrate film, cellulose acetate film, polyvinyl acetal resin film, paper or metal.

Photographic silver halide emulsions useful in my invention can also contain such addenda as chemical sensitizers, e.g., sulfur sensitizers (e.g., allyl thiocarbamide, thiourea, allyl isothiocyanate, cystine, etc.), various gold compounds (e.g., potassium chloroaurate, auric trichloride, etc.) (see U.S. Patents 2,540,085; 2,597,856 and 2,597,915), various azaindene compounds (such as those disclosed in U.S. Patent 2,716,062), condensation products of alkylene oxides, such as those shown in U.S. Patent 2,400,532, as well as the additives mentioned in Jones et al. U.S. application Serial No. 575,160, filed March 30, 1956 (now U.S. Patent 2,937,089, issued May 17, 1960).

As mentioned above, the advantages of my invention are particularly outstanding in reversal color photographic processes wherein the color-forming compound, or coupler, is incorporated in one of the developing baths. Couplers or color-forming compounds which are soluble in the strongly alkaline developing solutions are well known to those skilled in the art. Typical couplers include the following:

COUPLERS FOR USE IN COLOR DEVELOPERS

Cyan couplers

(1) 5-benzenesulfonamino-1-naphthol
(2) 2,4-dichloro-5-benzenesulfamino-1-naphthol
(3) 2,4-dichloro-5-(p-toluenesulfamino)-1-naphthol
(4) 5-(1,2,3,4-tetrahydronaphthalene-6-sulfonamino)-1-naphthol
(5) 2,4-dichloro-5-(4'-bromodiphenyl-4-sulfonamino)-1-naphthol
(6) o-(β-Naphthalenesulfonamino)-phenol
(7) 5-(m-nitrobenzenesulfonamino)-1-naphthol
(8) 5-(quinoline-5-sulfonamino)-1-naphthol (U.S. 2,362,598)
(9) 2-acetylamino-5-methylphenol
(10) 2-benzoylamino-3,5-dimethylphenol
(11) 2-α-(p-tert. amylphenoxy)-n-butyrylamino-5-methylphenol
(12) 2-α-(p-tert. amylphenoxy)-n-butyrylamino-4-chloro-5-methylphenol
(13) 2-(p'-tert. amylphenoxy-p-benzoyl)amino-4-chloro-5-methylphenol
(14) 2-(4''-tert. amyl-3'-phenoxybenzoylamino)-3,5-dimethyl-1-phenol
(15) 2-phenylacetylamino-4-chloro-5-methylphenol
(16) 2-benzoylamino-4-chloro-5-methylphenol
(17) 2-anilinoacetylamino-4-chloro-5-methylphenol
(18) 2-{4'-[α-(4''-tert. amylphenoxy)-n-butyrylamino]-benzoylamino}-4-chloro-5-methylphenol
(19) 2-{4'-[3''-(4'''-tert. amylphenoxy)-benzoylamino]-benzoylamino}-4-chloro-5-methylphenol
(20) 2-p-nitrobenzoylamino-4-chloro-5-methylphenol
(21) 2-m-aminobenzoyl-4-chloro-5-methylphenol
(22) 2-acetamino-4-chloro-5-methylphenol
(23) 2-(4'-sec. amylbenzamino)-4-chloro-5-methylphenol
(24) 2-(4'-n-amyloxybenzamino)-4-chloro-5-methylphenol

Magenta couplers

(25) 1-phenyl-3-acetylamino-5-pyrazolone
(26) 1-phenyl-3-propionylamino-5-pyrazolone
(27) 1-phenyl-3-dichloroacetylamino-5-pyrazolone
(28) 1-phenyl-3-benzoylamino-5-pyrazolone
(29) 1-phenyl-3-(m-aminobenzoyl)-amino-5-pyrazolone hydrochloride
(30) 1-phenyl-3-(diamylbenzoyl)amino-5-pyrazolone
(31) 1-phenyl-3-phenylcarbamylamino-5-pyrazolone
(32) 1-phenyl-3-phenoxyacetylamino-5-pyrazolone
(33) 1-phenyl-3-p-aminobenzoylamino-5-pyrazolone
(34) 1-phenyl-3-(o-carboxybenzoyl)amino-5-pyrazolone
(35) 1-phenyl-3-palmitylamino-5-pyrazolone
(36) 1-phenyl-3-(p-sec. amylbenzenesulfonylamino)-5-pyrazolone
(37) 1-phenyl-3-[p-(p'-sec. amylbenzoyl)aminobenzoylamino]-5-pyrazolone
(38) 1-m-tolyl-3-[m-(β-phenylpropionyl)aminobenzoylamino]-5-pyrazolone
(39) 1-m-tolyl-3-(2,4-di-tert. butyl-m-tolyloxyacetylamino)-5-pyrazolone
(40) 1-[p-(p'-tert. butylphenoxy)phenyl]-3-[p-(benzoylamino)-benzoylamino]-5-pyrazolone
(41) 1-(p-tert. butylphenoxyphenyl)-3-(p-n-amyloxybenzoylamino)-5-pyrazolone
(42) 1-[p-(p'-tert. butylphenoxy)phenyl]-3-(3,5-di-methoxybenzoyl)amino-5-pyrazolone
(43) 1-[p-(p'-tert. butylphenoxy)phenyl]-3-[m-(p-toluenesulfonylamino)benzoylamino]-5-pyrazolone
(44) 1-[p-(3,5-dimethylphenoxy)phenyl]-3-(4-n-amyloxy-3-methylbenzoylamino)-5-pyrazolone
(45) 3-(p-nitrophenoxyacetylamino)-1-(2,4,6-trichlorophenyl)-5-pyrazolone

Yellow couplers

(46) p-(ω-Benzoylacetamino)benzenesulfonamide
(47) p-(ω-Benzoylacetamino)benzenesulfon-N-methylamide
(48) p-(ω-Benzoylacetamino)benzenesulfonanilide
(49) 4-benzenesulfonamino-ω-benzoylacetanilide

(50) 4-(p-toluenesulfonamino)-ω-benzoylacetanilide

(51) 4-(p-laurylbenzenesulfonamino) - ω - benzoylacetanilide

(52) 1,4-di-[p-(benzoylacetamino)benzenesulfonamino]benzene

(53) N,N'-di-(p-benzoylacetaminophenyl)benzene - 1,3-disulfonamide

(54) N-(p-benzoylacetaminophenyl)-4-[p-(benzoylacetamino)-benzenesulfonamido]benzenesulfonamide

(55) N[4] - benzoylacetyl-N'-(2 - benzothiazolyl)sulfanilamide

(56) p-Acetoacetaminobenzenesulfon-β-naphthalide

(57) p - Furoylacetaminobenzenesulfon - N - cyclohexylamide

(58) p-(4-ethoxybenzoylacetamino)benzenesulfonamide

(59) terephthaloyl-bis[(p-N-amylsulfonamido)acetanilide]

(60) p-Quinoline-8-sulfonamino)-ω-benzoylacetanilide

(61) p-Acetoacetamino-o-methylbenzenesulfon-N-anilide

(62) N,N' - di-(p-benzoylacetaminophenol)naphthalene-1,5-disulfonamide

(63) p-(Benzenesulfonamino)benzoylacetone

(64) N-benzoylaceto-o-anisidine

Typical couplers that are primarily useful in the photographic silver halide emulsion layers of my invention comprise the following:

Coupler:

(65) 1 - hydroxy-2-[Δ-(2',4'-di-tert.amylphenoxy)-n-butyl]-naphthamide (U.S. Patent 2,474,293)

(66) 1-hydroxy - 4 - phenylazo-4'-(p-tert.-butylphenoxy)-2-naphthanilide (U.S. Patent 2,521,908)

(67) 2 - (2,4-di-tert.amylphenoxyacetamino)-4,6-dichloro-5-methylphenol (U.S. Patent 2,725,291)

(68) 2-(α-di-tert.amylphenoxy-n-butyrylamino)-4,6-dichloro-t-methylphenol

(69) 6-{α-{4-[α-(2,4-di-tert.amylphenoxy)butyramido]phenoxy}acetamido}-2,4-dichloro - 3 - methylphenol

(70) 2-[3' - (2",4" - diamylphenoxy) - acetamido]-benzamido-4-chloro-5-methylphenol

(71) 1 - (2',4',6'-trichlorophenyl)-3-[3"-(2"',4"'-di-tert.amylphenoxyacetamido) - benzamido] - 5-pyrazolone (U.S. Patent 2,600,788)

(72) 1 - (2',4',6'-trichlorophenyl)-3-[3"-(2"',4"'-di-tert.amylphenoxyacetamido)-benzamido] - 4 - (p-methoxyphenylazo)-5-pyrazolone

(73) N-(4-benzoylacetaminobenzenesulfonyl)-N-(γ-phenylpropyl)-p-toluidine (U.S. Patent 2,298,443)

(74) α-o-methoxybenzoyl-α-chloro-4-[α-(2,4-di-tert.-amylphenoxy) - n - butyramido]-acetanilide (McCrossen U.S. Patent 2,728,658)

(75) α - {3-[α-(2,4-di-tert.amylphenoxy)acetamido]-benzoyl}-2-methoxyacetanilide

(76) 3-benzoylacetamido - 4 - methoxy-2',4'-di-tert.-amylphenoxyacetanilide

(77) 4-benzoylacetamido - 3 - methoxy-2',4'-di-tert.-amylphenoxyacetanilide

Other couplers suitable for use in the emulsions of my invention comprise those disclosed in Spence and Carroll U.S. Patent 2,640,776, issued June 2, 1953; Weissberger et al. U.S. Patent 2,407,210, issued September 3, 1946; and Weissberger et al. U.S. Patent 2,474,293, issued June 28, 1949.

The color-forming developers useful in my invention have been previously described in the prior art, and my invention is not to be restricted to the use of any particular color-forming developer. The color-forming developers previously mentioned which I have found to be especially useful in my invention comprise aromatic primary amines containing an amino (substituted or not) or hydroxyl substituent. Phenylenediamines and substituted derivatives thereof containing a primary amino group have been found to provide excellent results when employed in combination with the heterocyclic compounds of my invention. Typical of such color-forming developers are the sulfonamido substituted p-phenylenediamines disclosed in Weissberger U.S. Patent 2,548,574, issued April 10, 1951, the substituted p-phenylenediamines disclosed in Weissberger et al. U.S. Patent 2,566,271, issued August 28, 1951. Other phenylenediamine color-forming developers can be employed to like advantage in the process of my invention.

The first developer employed in the process of my invention is generally a rapid developer of the MQ type, i.e., a combination of hydroquinone and Elon (p-N-methylaminophenol) developer.

The photographic silver halide emulsions useful in the process of my invention can be prepared according to known methods, such as those described in Hewitson and McClintock U.S. Patent 2,618,556, issued November 18, 1952, for example. Of course, emulsions prepared by other methods can be used to equal advantage in my invention. These emulsions can be chemically sensitized or not, as mentioned above. Additional chemical sensitizers useful in my invention comprise those disclosed in the copending application Serial No. 550,495, filed December 1, 1955 (now U.S. Patent 2,886,437, issued May 12, 1959), in the name of D. E. Piper.

The following examples will serve to illustrate more fully the manner of practicing my invention.

Example 1.—A portion of a gelatino-silver-bromiodide emulsion which had been sensitized with a sulfur compound and a gold compound as mentioned above was coated on a cellulose acetate support. The coating was then cut into several strips, identified coating series A below. The oleyl ether of a polyethyleneglycol having a molecular weight greater than 300 was added to a second portion of the same emulsion at a concentration of 5 gms. of the oleyl ether per mole of silver halide, and the emulsion coated onto a cellulose acetate support. The dried coating was then cut into several strips, identified as coating series B below. One strip of each coating was exposed for 1/25 second to a 500-watt, 3000° K. light source on an Eastman Type I*b* sensitometer. The exposed coatings were then developed for 3 minutes in a developer having the following composition:

Sodium hexametaphosphate	g	0.5
Sodium sulfite (anhydrous)	g	40.0
N-methyl-p-aminophenolsulfate	g	5.0
Hydroquinone	g	2.0
Sodium carbonate (monohydrate)	g	25.0
Potassium bromide	g	1.0
Potassium iodide (0.1% solution)	cc	2

Water to make one liter.
(pH was 10.1 at 70° F.)

The coatings were then washed for two minutes.

Color development.—The above coatings were given a reversal exposure for about 10 seconds (flash) with a No. 2 Photoflood set at a distance of 60 inches. The coatings were developed to an adequate D-max. (time=5 minutes) in a developer having the following formula:

Sulfuric acid (conc.)	cc	1.0
Sodium hexametaphosphate	g	0.5
Sodium sulfite (anhydrous)	g	5.0
Color developer [1]	g	0.6
Sodium carbonate (monohydrate)	g	15.0
Potassium bromide	g	0.25
Potassium iodide (0.1% solution)	cc	2
Coupler [2]	g	1.2
Sodium hydroxide	g	0.3

Water to make one liter.

[1] 4-amino-3-methyl-N,N-diethylaniline hydrochloride.
[2] 2,4-dichloro-5-(p-toluenesulfonamido)-1-naphthol.

The coatings were washed for ten minutes and treated for two minutes in a silver bleach bath having the following composition:

Potassium ferricyanide ____ g__	100
Potassium bromide ____ g__	10
Borax ____ g__	7.5
Boric acid ____ g__	5.0
Water to make one liter.	

The coatings were then treated for two minutes in a fixing bath having the composition given below, washed and dried.

Sodium thiosulfate (pentahydrate) ____ g__	200
Sodium sulfite (anhydrous) ____ g__	10
Water to make one liter.	

In order to obtain cyan fog readings, an additional strip of each coating was put through the same process except that the flash re-exposure was omitted. The D-max. and color (cyan) fog for each of the coatings were then measured, the results being given below.

Additional strips of coated emulsions were processed exactly as described above except that a heterocyclic compound, as identified above, and in the quantity given in the following table, was added to the color developer. The D-max. and cyan fog for each of these coatings were also measured, the results being given in the following table.

Compound No.	Conc., g./liter	Coating Series A		Coating Series B	
		D-max.	Cyan Fog	D-max.	Cyan Fog
Control	none	3.40	0.18	3.30	0.31
1	0.25	3.20	.02	3.50	.10
2	.30	2.70	.08	3.00	.14
3	.006	2.90	.13	3.50	.12
4	.15	3.40	.06	3.30	.09
5	.06	3.50	.12	3.90	.23
6	.15	2.90	.10	3.20	.14

The improvement obtained as a result of the use of the heterocyclic compounds of my invention is immediately apparent, in emulsions with or without a polyethyleneglycol derivative. While color density is maintained at a high level, the color fog was materially reduced.

The heterocyclic compounds useful in practicing my invention can also be used during magenta and yellow development, as indicated above. For example, Compound 1 can be employed in color developers containing color-forming compounds for the magenta image, such as Coupler No. 45. Complete directions for such a technique are illustrated in Example 2 of my copending application Serial No. 635,944, filed January 24, 1957 (now U.S. Patent 2,899,306, issued August 11, 1959). In like manner, the heterocyclic compounds of my invention, such as Compound 1, can be employed in color developers containing a color-forming compound for the yellow image, such as Coupler No. 64 above. Complete directions for such a technique can be found in Example 3 of my copending application Serial No. 635,944 mentioned above.

While it has been previously proposed to add various mercapto compounds to color developers, such compounds fail to maintain color density at a high level, although they do reduce color fog. For example, processing of an emulsion having the same compoistion as coating B of Example 1, the same developing compositions shown in Example 1 being used, except that 0.01 g./liter of 1-phenyl-5-mercaptotetrazole was added to the color developer in place of the compound of Example 1, gave the following results:

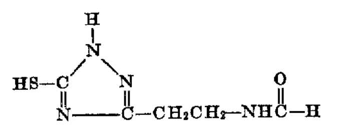
	Color Development, min.	D-max.	Cyan Fog
Control	4	3.30	0.31
1-phenyl-5-mercaptotetrazole	5	1.42	0.10

While the above mercapto compound did reduce the cyan fog to one-third the level of the coating treated with a color developer containing no antifoggant, it also caused a density loss of more than one-half.

While the above examples primarily illustrate the use of photographic emulsions which have been sensitized with the oleyl ether of polyethylene glycol, it is to be understood that other condensates of alkylene oxides can be advantageously employed to sensitize such emulsions. Such condensates are generally referred to as alkylene oxide polymers, the alkylene oxides generally containing from 2 to 4 carbon atoms. Such alkylene oxide polymers include polyalkylene glycols and condensation products of alkylene oxides with organic compounds containing an active hydrogen atom, such as alcohols, amines, mercaptans, acids, amides, etc. Generally, such alkylene oxide polymers have a molecular weight of at least 300, as shown in U.S. application Serial No. 550,495, mentioned above. It is to be further understood that the emulsions employed in my invention need not be sensitized, although particularly useful results have been obtained with emulsions which have been sensitized with such alkylene oxide polymers.

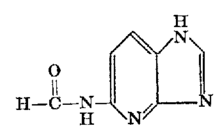
I have also found that a number of other organic compounds can conveniently be employed in the methods of my invention for processing multilayer color films or selectively sensitized color materials, such as mixed packet color materials. These compounds can be represented by the following formulas:

(7)



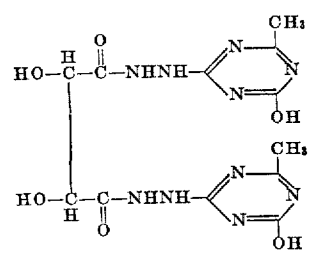
3-β-formamidoethyl-5-mercapto-1,2,4-triazole

(8)



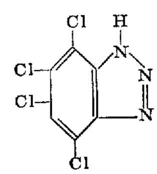
5-formamido-1,3,4-triazaindene

(9)



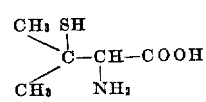
Tartaric bis[β-(4-hydroxy-6-methylpyrimid-2-yl)]hydrazide

(10)



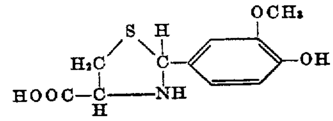
Tetrachlorobenzotriazole (1,2,3)

(11)



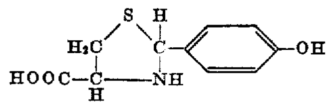
α-Amino-β-mercaptoisovaleric acid

(12)



2-(4-hydroxy-3-methoxyphenyl)-4-carboxythiazolidine

(13)



2-(4-hydroxyphenyl)-4-carboxythiazolidine

The above compounds (i.e., 7–13) were tested in an ordinary gelatino-silver-bromiodide emulsion in exactly the manner described in Example 1 above. The tests were made both in an emulsion containing no oleyl ether sensitizer and in emulsions containing the oleyl ether sensitizer used in Example 1. The processing used was exactly the same as that described in detail in Example 1. The results were as follows:

Compound No.	Conc., g./liter	Coating Series A		Coating Series B	
		D-max.	Cyan Fog	D-max.	Cyan Fog
Control	none	3.40	0.18	3.30	0.31
7	.01	----	----	3.20	0.14
8	.03	3.60	0.16	3.90	0.11
9	.75	3.60	0.05	3.50	0.22
10	.006	3.20	0.13	3.60	0.13
11	.3	3.30	0.10	3.30	0.12
12	.5	3.30	0.14	3.00	0.16
13	.3	----	----	4.00	0.14

As indicated above, many of the compounds useful in the method of my invention can be prepared according to methods previously described in the prior art. The following examples will serve to illustrate further the manner of preparing certain of these compounds.

Compound 3. — 6-hydroxy-3-mercapto-4-methyl-1,2,3a,7-tetrazaindene.—To a solution of 7 g. (0.05 mole) of 2-hydrazino-4-hydroxy-6-methylpyrimidine in 2 l. of hot ethanol were added 7 g. (0.052 mole) of phenylisothiocyanate and the mixture allowed to stand at room temperature overnight. The solid was collected by filtration and recrystallized from water to give 5 g. of the azaindene, M.P. 278° C.

Analysis.—Calc'd. for $C_6H_6N_4OS$: C, 39.1; H, 3.3; N, 30.7; S, 17.5. Found: C, 39.6; H, 3.7; N, 31.1; S, 18.5.

Compound 4.—4-hydroxy-2-mercaptomethyl-6-methyl-1,3,3a,7-tetrazaindene. — Treatment of 2-formamidinothiomethyl-4-hydroxy-6-methyl - 1,3,3a,7 - tetrazaindene with boiling dilute aqueous caustic soda, followed by acidification and recrystallization from water, yields this material, M.P. 255–259° C.

Analysis.—Calc'd: C, 42.8; H, 4.1; S, 16.3. Found: C, 42.8; H, 4.3; S, 16.6.

Compound 6.—7-amino - 5-mercapto - 1,2,3,4,6 - pentazaindene.—Sixteen grams (0.098 mole) of 2-mercapto-4,5,6-triamino pyrimidine sulfate were suspended in 200 ml. of water and dissolved by the addition of sodium hydroxide. The solution was filtered and to the filtrate were added 7 g. (0.1 mole) of sodium nitrite. The resulting solution was acidified by the addition of acetic acid and heated on the steam bath for one-half hour. The mixture was cooled in an ice bath, the solid collected, and dissolved in sodium hydroxide solution. The solution was then filtered through Norite (activated carbon) and the filtrate acidified with acetic acid. The solid was collected, washed thoroughly with water, and dried overnight to give eight grams of product (M.P. 300° C.). The 2-mercapto-4,5,6-triamino pyrimidine sulfate was prepared according to the method described in JACS 70, 3111 (1948).

Compound 7. — 3-β-formamidoethyl-5-mercapto-1,2,4-triazole.—A solution of 5 g. (0.035 mole) of 3-β-aminoethyl-5-mercapto-1,2,4-triazole (JACS 75, 4915 (1953)) in 25 ml. of 98 percent formic acid was refluxed 5 hours and then evaporated to dryness on the steam bath in vacuo. The colorless glass-like residue was triturated with a small amount of alcohol and the white crystalline material was recrystallized from aqueous ethanol to give 2 g. of the amide as the hydrate, M.P. 202–3° C.

Analysis.—Calc'd. for $C_5H_{10}N_4SO_2$; C, 31.7; H, 5.3; N, 29.5. Found: C, 31.8; H, 5.4; N, 28.9.

Compound 8. — 5-formamido-1,3,4-triazaindene. — A mixture of 6.4 g. (0.04 mole) of 2,3,6-triaminopyridine hydrochloride and 4.5 g. (0.066 mole) of sodium formate in 65 ml. of 98 percent formic acid was refluxed 1.5 hours and then concentrated to dryness. The solid residue was washed with water and recrystallized from a small volume of 50 percent acetic acid or from 95 percent ethanol to yield 2.5 g. of 5-formamido-1,3,4-triazaindene (M.P. 257–9° C.; reported M.P. 256–8° C.).

Compound 9. — Tartaric bis-β-(4-hydroxy-6-methyl-2-pyrimidyl)-hydrazide.—A mixture of 178 g. (1 mole) of tartaric hydrazide (prepared according to Berichte, 26, 2058 and JACS 83, 1363), 340 g. (2 moles) of 2-ethylmercapto-4-hydroxy - 6 - methylpyrimidine (prepared according to Birr, Berichte, 86, 1403), and one l. of water heated on the steam bath for 20 hours, cooled to 25°, and filtered. This crude product weighed 263 g., 67 percent, M.P. 263–288° C. with decomposition. It was digested thoroughly with 2 l. of boiling water, cooled to 25° C. and filtered, yielding 219 g., 56 percent, of product, M.P. 281–285° C. dec. (infrared absorption curve 7270 A.).

Compounds 1 and 2 were prepared according to the method described in "JACS," vol. 78 (1956), page 159. Compound 5 was prepared according to the method described in "JACS," vol. 74 (1952), page 411. Compound 10 was prepared according to the method described in "JACS," vol. 77 (1955), page 5105. Compounds 12 and 13 were prepared according to the method described in my copending application Serial No. 602,067, filed August 3, 1956 (now U.S. Patent 2,860,936, issued November 18, 1958).

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

1. A photographic developer for color photography comprising an aqueous alkaline solution of an aromatic primary amine developing agent containing, in addition to the primary amine group, a substituent selected from the group consisting of hydroxyl and an amino group, an alkali metal sulfite and at least 5 mg. per liter of solution of an organic heterocyclic compound selected from those represented by the following general formula:

$$R—(CH_2)_{n-1}—SM$$

wherein R represents a member selected from the group consisting of a tetrazaindenyl group and a pentazaindenyl group, *n* represents a positive integer of from 1 to 2 and M represents a member selected from the group consisting of a hydrogen atom and an alkali metal atom.

2. A photographic developer for color photography comprising an aqueous alkaline solution of an arylenediamine photographic developing agent, an alkali metal sulfite and at least 5 mg. per liter of solution of a compound selected from those represented by the following general formula:

$$R—(CH_2)_{n-1}—SM$$

wherein R represents a member selected from the group consisting of a tetrazaindenyl group and a pentazaindenyl group, *n* represents a positive integer of from 1 to 2 and M represents a member selected from the group consisting of a hydrogen atom and an alkali metal atom.

3. A photographic developer for color photography comprising an aqueous alkaline solution of a p-phenylenediamine photographic developing agent, an alkali metal sulfite and at least 5 mg. per liter of solution of a compound selected from those represented by the following general formula:

$$R—(CH_2)_{n-1}—SM$$

wherein R represents a member selected from the group consisting of a tetrazaindenyl group and a pentazaindenyl group, *n* represents a positive integer of from 1 to 2 and M represents a member selected from the group consisting of a hydrogen atom and an alkali metal atom.

4. A developing composition for color photography comprising an aqueous alkaline solution of a p-phenylenediamine color developer, an alkali metal sulfite and at least 5 mg. per liter of solution of a compound selected from those represented by the following general formula:

R—SM

wherein R represents a tetrazaindenyl group and M represents a member selected from the group consisting of a hydrogen atom and an alkali metal atom.

5. An aqueous developing solution for color photography comprising a p-phenylenediamine color developer, an alkali metal sulfite, a color-forming compound capable of coupling with the oxidation products of said p-phenylenediamine color developer and at least 5 mg. per liter of solution of a compound selected from those represented by the following general formula:

R—SM

wherein R represents a tetrazaindenyl group and M represents a member selected from the group consisting of a hydrogen atom and an alkali metal atom.

6. A photographic developer for color photography comprising an aqueous alkaline solution of a p-phenylenediamine photographic developing agent, an alkali metal sulfite and at least 5 mg. per liter of 4,7-dihydroxy-2-mercapto-1-phenyl-1,3,5,6-tetrazaindene.

7. A photographic developer for color photography comprising an aqueous alkaline solution of a p-phenylenediamine photographic developing agent, an alkali metal sulfite and at least 5 mg. per liter of 6-hydroxy-3-mercapto-4-methyl-1,2,3a,7-tetrazaindene.

8. A photographic developer for color photography comprising an aqueous alkaline solution of a p-phenylenediamine photographic developing agent, an alkali metal sulfite and at least 5 mg. per liter of 4-hydroxy-2-mercaptomethyl-6-methyl-1,3,3a,7-tetrazaindene.

9. A photographic developer for color photography comprising an aqueous alkaline solution of a p-phenylenediamine photographic developing agent, an alkali metal sulfite and at least 5 mg. per liter of 7-mercapto-1,3,4,6-tetrazaindene.

10. A photographic developer for color photography comprising an aqueous alkaline solution of a p-phenylenediamine photographic developing agent, an alkali metal sulfite and at least 5 mg. per liter of 7-amino-5-mercapto-1,2,3,4,6-pentazaindene.

11. In a complete photographic reversal color process wherein a multilayer photographic element containing a plurality of differentially sensitized photographic silver halide emulsion layers is given a first exposure, followed by development in a photographic developer for producing a black-and-white negative image and a second exposure, followed by at least one additional development in a photographic developer for producing a colored image, said colored image bearing a complementary relationship to the region of the spectrum to which said photographic silver halide emulsion has been differentially sensitized, the improvement which consists in producing the said colored image by developing in a color developer comprising an aromatic primary amine developing agent containing a substituent in addition to the amine group selected from the group consisting of hydroxyl and an amino group, and at least 5 mg. per liter of solution of an organic compound selected from those represented by the following general formula:

$$R-(CH_2)_{n-1}-SM$$

wherein R represents a member selected from the group consisting of a tetrazaindenyl group and a pentazaindenyl group, n represents a positive integer of from 1 to 2 and M represents a member selected from the group consisting of a hydrogen atom and an alkali metal atom.

12. In a complete photographic reversal color process wherein a multilayer photographic element containing a plurality of differentially sensitized photographic silver halide emulsion layers is given a first exposure, followed by development in a photographic developer for producing a black-and-white negative image and a second exposure, followed by at least one additional development in a photographic developer for producing a colored image, said colored image bearing a complementary relationship to the region of the spectrum to which said photographic silver halide emulsion has been differentially sensitized, the improvement which consists in producing the said colored image by developing the exposed photographic silver halide emulsion in a color developer comprising a p-phenylenediamine color developer, an alkali metal sulfite and at least 5 mg. per liter of solution of a compound selected from those represented by the following general formula:

$$R-(CH_2)_{n-1}-SM$$

wherein R represents a member selected from the group consisting of a tetrazaindenyl group and a pentazaindenyl group, n represents a positive integer of from 1 to 2 and M represents a member selected from the group consisting of a hydrogen atom and an alkali metal atom.

13. In a complete photographic reversal color process wherein a multilayer photographic element containing a plurality of differentially sensitized photographic silver halide emulsion layers is given a first exposure, followed by development in a photographic developer for producing a black-and-white negative image and a second exposure, followed by at least one additional development in a photographic developer for producing a colored image, said colored image bearing a complementary relationship to the region of the spectrum to which said photographic silver halide emulsion has been differentially sensitized, the improvement which consists in producing the said colored image by developing the exposed photographic silver halide emulsion in a color developer comprising a p-phenylenediamine color developer, an alkali metal sulfite, a color-forming compound capable of coupling with the oxidation products of said p-phenylenediamine color developer, and at least 5 mg. per liter of solution of a compound selected from those represented by the following general formula:

$$R-(CH_2)_{n-1}-SM$$

wherein R represents a member selected from the group consisting of a tetrazaindenyl group and a pentazaindenyl group, n represents a positive integer of from 1 to 2 and M represents a member selected from the group consisting of a hydrogen atom and an alkali metal atom.

14. In a complete photographic reversal color process wherein a multilayer photographic element containing a plurality of differentially sensitized photographic silver halide emulsion layers is given a first exposure, followed by development in a black-and-white negative developer containing hydroquinone and N-methyl-p-aminophenol sulfate, and a second exposure followed by at least one additional development in a photographic developer for producing a colored image, said colored image bearing a complementary relationship to the region of the spectrum to which the photographic silver halide emulsion has been differentially sensitized, the improvement which consists in producing the said colored image by developing said exposed silver halide emulsion in a developer comprising alkali, a p-phenylenediamine color developer, a color-forming compound capable of coupling with the oxidation products of said p-phenylenediamine color developer, and at least 5 mg. per liter of solution of a compound selected from those represented by the following general formula:

R—SM

wherein R represents a tetrazaindenyl group and M represents a member selected from the group consisting of a hydrogen atom and an alkali metal atom.

15. In a complete photographic reversal color process wherein a multilayer photographic element containing a

plurality of differentially sensitized photographic silver halide emulsion layers is given a first exposure, followed by development in a photographic developer for producing a black-and-white negative image and a second exposure, followed by at least one additional development in a photographic developer for producing a colored image, said colored image bearing a complementary relationship to the region of the spectrum to which said photographic silver halide emulsion has been differentially sensitized, the improvement which consists in producing the said colored image by developing said exposed photographic silver halide emulsion in a developer comprising a p-phenylenediamine color developer, an alkali metal sulfite, a color-forming compound capable of coupling with the oxidation products of said p-phenylenediamine color developer and at least 5 mg. per liter of solution of 4,7-dihydroxy-2-mercapto-1-phenyl-1,3,5,6-tetrazaindene.

16. In a complete photographic reversal color process wherein a multilayer photographic element containing a plurality of differentially sensitized photographic silver halide emulsion layers is given a first exposure, followed by development in a photographic developer for producing a black-and-white negative image and a second exposure, followed by at least one additional development in a photographic developer for producing a colored image, said colored image bearing a complementary relationship to the region of the spectrum to which said photographic silver halide emulsion has been differentially sensitized, the improvement which consists in producing the said colored image by developing said exposed photographic silver halide emulsion in a developer comprising a p-phenylenediamine color developer, an alkali metal sulfite, a color-forming compound capable of coupling with the oxidation products of said p-phenylenediamine color developer and at least 5 mg. per liter of solution of 6-hydroxy-3-mercapto-4-methyl-1,2,3a,7-tetrazaindene.

17. In a complete photographic reversal color process wherein a multilayer photographic element containing a plurality of differentially sensitized photographic silver halide emulsion layers is given a first exposure, followed by development in a photographic developer for producing a black-and-white negative image and a second exposure, followed by at least one additional development in a photographic developer for producing a colored image, said colored image bearing a complementary relationship to the region of the spectrum to which said photographic silver halide emulsion has been differentially sensitized, the improvement which consists in producing the said colored image by developing said exposed photographic silver halide emulsion in a developer comprising a p-phenylenediamine color developer, an alkali metal sulfite, a color-forming compound capable of coupling with the oxidation products of said p-phenylenediamine color developer and at least 5 mg. per liter of solution of 4 - hydroxy - 2 - mercaptomethyl - 6 - methyl - 1,3,3a,7-tetrazaindene.

18. In a complete photographic reversal color process wherein a multilayer photographic element containing a plurality of differentially sensitized photographic silver halide emulsion layers is given a first exposure, followed by development in a photographic developer for producing a black-and-white negative image and a second exposure, followed by at least one additional development in a photographic developer for producing a colored image, said colored image bearing a complementary relationship to the region of the spectrum to which said photographic silver halide emulsion has been differentially sensitized, the improvement which consists in producing the said colored image by developing said exposure photographic silver halide emulsion in a developer comprising a p-phenylenediamine color developer, an alkali metal sulfite, a color-forming compound capable of coupling with the oxidation products of said p-phenylenediamine color developer and at least 5 mg. per liter of solution of 7-mercapto-1,3,4,6-tetrazaindene.

19. In a complete photographic reversal color process wherein a multilayer photographic element containing a plurality of differentially sensitized photographic silver halide emulsion layers is given a first exposure, followed by development in a photographic developer for producing a black-and-white negative image and a second exposure, followed by at least one additional development in a photographic developer for producing a colored image, said colored image bearing a complementary relationship to the region of the spectrum to which said photographic silver halide emulsion has been differentially sensitized, the improvement which consists in producing the said colored image by developing said exposed photographic silver halide emulsion in a developer comprising a p-phenylenediamine color developer, an alkali metal sulfite, a color-forming compound capable of coupling with the oxidation products of said p-phenylenediamine color developer and at least 5 mg. per liter of solution of 7-amino-5-mercapto-1,2,3,4,6-pentazaindene.

References Cited in the file of this patent

UNITED STATES PATENTS

2,675,314	Vittum et al.	Apr. 13, 1954
2,713,541	Allen et al.	July 19, 1955
2,743,181	Allen et al.	Apr. 24, 1956